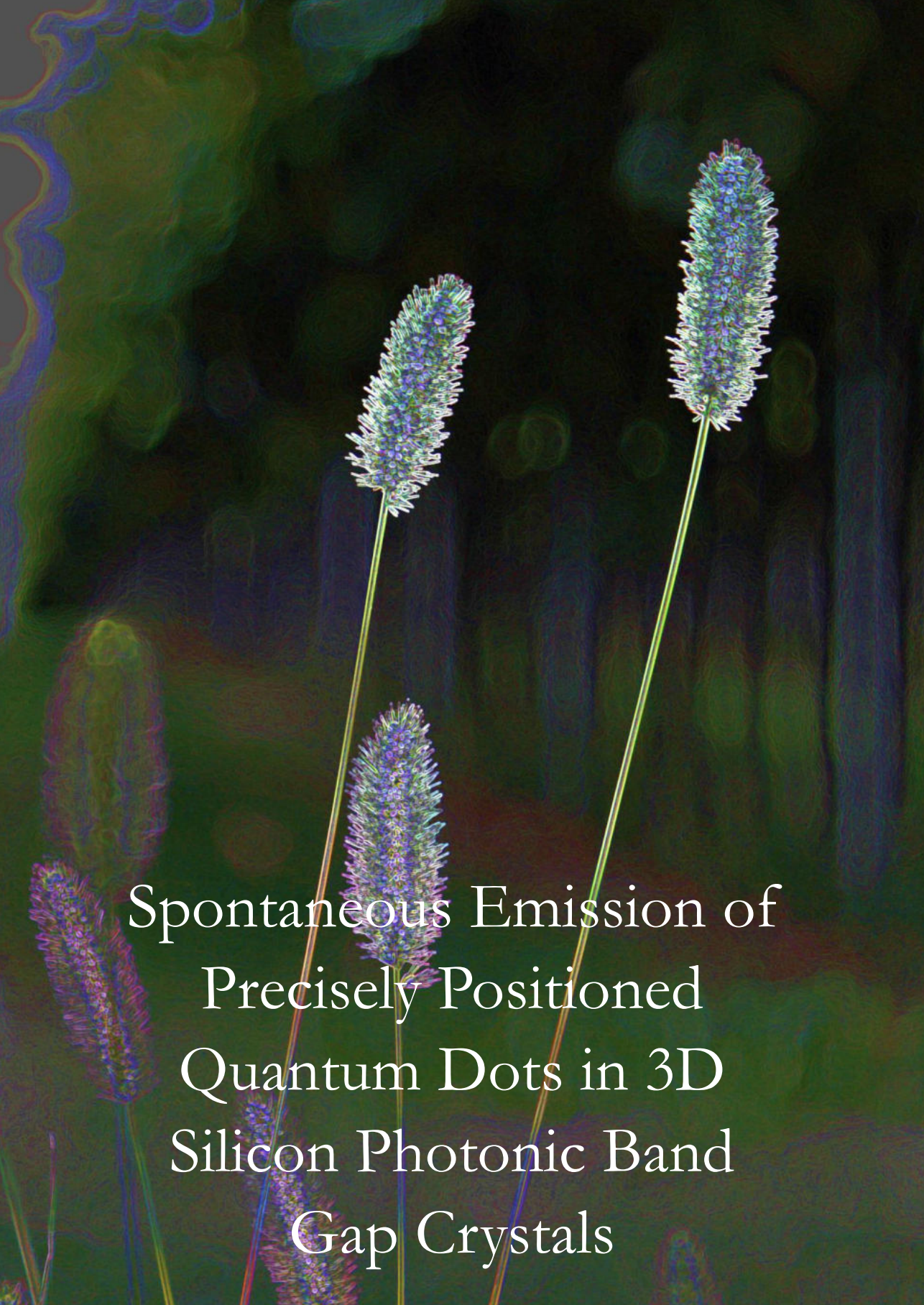


The background of the slide is a dark, textured image of several lavender flower spikes. The flowers are a vibrant purple color, and the stems are thin and green. The background has a mottled, almost painterly quality with shades of dark green, blue, and black.

Spontaneous Emission of Precisely Positioned Quantum Dots in 3D Silicon Photonic Band Gap Crystals

**SPONTANEOUS EMISSION OF
PRECISELY POSITIONED
QUANTUM DOTS IN 3D
SILICON PHOTONIC BAND
GAP CRYSTALS**

Andreas Stefan Schulz

SPONTANEOUS EMISSION OF PRECISELY POSITIONED QUANTUM DOTS IN 3D SILICON PHOTONIC BAND GAP CRYSTALS

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
prof.dr.ir. A. Veldkamp,
on account of the decision of the Doctorate Board,
to be publicly defended
on Friday the 14th of March 2025 at 10:45

by

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in Dortmund, Germany.

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prof.dr. G.J. Vancso

Cover design: Artist's impression of polymer brushes grafted from the silicon-air interfaces of 3D silicon photonic crystal pores. The parallel periodic lines of the vines represent the pore walls of the photonic crystal. In the foreground, individual grasses (species "Pennisetum alopecuroides" or "foxtail fountain grass") represent the polymer chains. The flower spikes illustrate the reactive side chains with the attached quantum dots. At the top center, a mode cavity is visible due to imperfections in the crystal. The tips of the grasses glow from the excited quantum dots emitting light, but the rest of the photonic crystal volume remains dark. The scientifically correct size ratio between the polymer chains and the quantum dots is not taken into account in the artwork. The artwork is called "*Flos felix - Lata disposita velut vinea*". Concept and design by Andreas Stefan Schulz.

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In memoriam of
my beloved father **Alf**

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CHAPTER 1

Introduction

1.1 General introduction

Warm summer evenings we like to spend outside with our loved ones, watching the cloudless sky and gazing at the stars after the sunset. Both the stars in the cosmos and the Moon, which is closer to our planet Earth, appear clearly in the sky. Our nearby star, the Sun, illuminates the Moon and the planets of our solar system, and the other stars farther away behave similarly, so the sky is not completely dark. Light is a fascinating phenomenon because we cannot grasp it directly. Most of the light on Earth and in the Universe is emitted spontaneously, as will be studied in this thesis. By illuminating different objects on Earth, we see colors and shapes. Without light, life on Earth as we know it would not exist because light is essential for many biological processes, the most important of which is photosynthesis. If humanity could capture and store light, we would be able to release it later. This would open up the possibility of sending information or energy through space for space exploration and to communicate with places far away from Earth or with our friends on nearby sunny balconies.

The use of light as a carrier of information and energy is already ubiquitous in everyone's daily life. Photovoltaic (PV) cells convert the energy of sunlight into electricity; this is an example of photochemistry because the light excites an upper energy state in a material that is quickly converted into an electric current. A more sophisticated energy conversion consists of transferring energy packets between excited states of nanoscale quantum dots (QDs), using nanotechnology to realize a new type of photochemistry, including applications in quantum information processing.

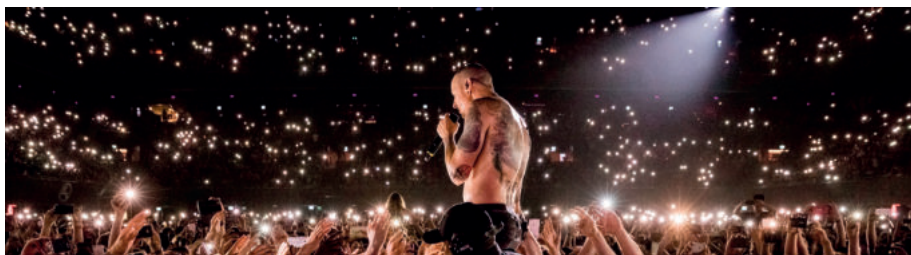


Figure 1.1: Chester Bennington in between his fans during the song “One More Light” by Linkin Park [1]. This photo was taken by LP family, image courtesy of LP family.

Today, data centers, especially those of Big Tech, process a huge amount of information for (tele-)communication, data storage and artificial intelligence. The need for faster and more efficient data transfer and processing is enormous to meet the ever-increasing information demands of the world's growing population. In the past, networking companies sent our data as electronic currents over long distances through copper wires. As the amount of data increased, the wires heated up as the electrons scattered off the ions in the wires, dissipating current, heating up, and impeding the flow of data. This property became such a problem that a new infrastructure for transmitting data was soon invented: light traveling through optical fibers [2, 3]. Using photons instead of electrons allows for much higher data transfer rates, since much more information can be processed simultaneously by modulating the high-frequency electromagnetic oscillations we know as light. In addition, data transmission over an optical fiber has a lower latency, is more energy efficient, and has a low attenuation rate, which means that the signal strength degrades very little over long distances. It is now possible to transmit optical signals at extremely high frequencies and at different wavelengths, allowing for higher data density transmissions.

Currently, we use silicon chips in our phones, laptops, and many other devices that use electrical signals to process data. If we use photons on a chip, the computing power of central processing units (CPUs) will be greatly increased, so this is actually being pursued worldwide [4]. The four main components of a photonic chip are light sources such as miniature light-emitting diodes and lasers, modulators, passive structures, and photodetectors. Of these four components, lasers and modulators are currently the subject of much scientific research to improve their performance in order to become economically and sustainably viable. Especially for miniature light sources, controlling the competition between spontaneous emission (see below) and stimulated emission is relevant, as well as controlling the emission in desired directions and polarizations. The research in this thesis deals with the control of spontaneous emission in exquisite detail and the exploitation of tailored nanophotonic structures made of silicon, and thus ultimately describes research directions that improve our control of on-chip emission.

1.2 Spontaneous emission

Light plays a central role in many devices, functions, and applications in our daily life. Luminescent materials such as phosphors are used in light-emitting diodes (LEDs) [6], organic molecules and polymers in organic light-emitting diodes (OLEDs) [7] and quantum dots in quantum dot-based LEDs (QD-LEDs) [8, 9] are employed in popular devices like television screens, liquid-crystal displays (LCDs), mobile phones, and tablet computers. In all these applications, various forms of energy - chemical, electrical, mechanical - are converted into electromagnetic energy. At relatively low frequencies (up to about tens or hundreds of GHz), the concomitant radio or microwaves are emitted by a macroscopic antenna, as illustrated in Figure 1.2, whose behavior is well described by classical electro-

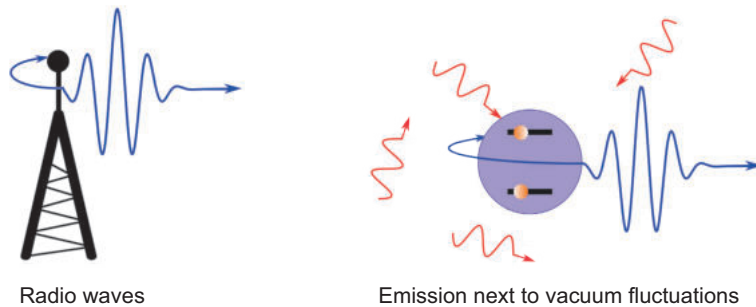


Figure 1.2: Illustrations of low-frequency radio wave emission (left) and high-frequency quantum emission (right). (Left) Emission from a classical antenna is described by the electrodynamic concept of radiation reaction, where the emitted field acts back on the antenna, pulling energy out of the current that flows up and down the antenna. (Right) The same process also happens during spontaneous emission from an atom, with the emitted radiation extracting energy from the oscillating charge. In addition, the emission is triggered by the presence of (quantum) vacuum fluctuations that induce emission from the upper level of the two-level emitter. In case of quantum emission, both radiation reaction and vacuum fluctuations contribute equally. Figure adapted from [5].

dynamics [5]. In this regime, electromagnetic oscillations are readily visualized with classical electronic devices like oscilloscopes.

At much higher frequencies, also known as the optical regime, the size of an elementary emitter (an excited atom, ion, molecule, quantum dot) is typically so much smaller than a wavelength that its properties are well described by quantum mechanics. In this regime, the emission of light by an elementary emitter is caused not only by (classical) antenna effects, but also by quantum electrodynamic effects, see Figure 1.2. These quantum effects involve omnipresent electromagnetic fluctuations that even exist in vacuum, also known as vacuum fluctuations or quantum fluctuations. Even in vacuum and in absence of any source of light (zero photons), the electric field fluctuates in time with a zero mean and non-zero root mean square. The vacuum fluctuations are temporal changes in the amount of energy at a point in space. While seemingly exotic or elusive, the fluctuations are encountered everyday in chemistry by their central role in dispersion, London, van der Waals, and Casimir forces [10]. The energy conversion from an excited emitter to light is referred to as luminescence.

In its simplest form, an elementary emitter is described by two quantized energy levels with concomitant wave functions, see Figure 1.3. The process by which an excited luminescent material transitions from an excited energy state E_e to a lower energy state E_g by emitting a photon, is spontaneous emission schematically shown in Figure 1.3. In the optical regime, oscillation frequencies are so high that electronic methods cannot detect the wave oscillations anymore, and detectors sense the electromagnetic energy as discrete packets of energy,

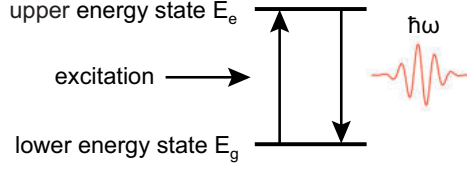


Figure 1.3: Schematic of a two level quantum emitter. The system is excited to an upper energy state E_e at $t' = 0$. At a random moment in time $t' = t$ it spontaneously makes a transition to a lower-energy ground state E_g by emitting a quantum $\hbar\omega$ in form of a photon.

known as photons [11], with energy quanta $\hbar\omega$.

Since it is impossible to determine *a priori* how long the emitter stays in the excited state before emitting a photon, the process is spontaneous. Using quantum optics, spontaneous emission is described by the interaction of an excited emitter with an electric field since even vacuum has an energy $\frac{1}{2}\hbar\omega$ per mode [12]. For an ensemble of emitters, *e.g.*, for a quantum dot suspension, where the process of spontaneous emission is repeated many times starting with repeated excitation by a pulse of an external light source, the distribution for the delayed emission events is well defined. The average time for an emitter to decay is known as the lifetime τ_{LF} . The inverse of the lifetime is the decay rate Γ . The radiative decay rate for dipole transitions is given by Fermi's Golden rule [13]

$$\Gamma_{\text{rad}}(\mathbf{r}) = \frac{2\pi}{\hbar} \sum_{|f\rangle} |\langle f | \hat{\mathbf{d}}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}) | i \rangle|^2 \delta((E_e - E_g) - \hbar\omega), \quad (1.1)$$

where $\hat{\mathbf{d}}$ is the transition dipole operator and r the position. The Dirac delta function $\delta(\cdot)$ expresses mathematically that energy is conserved. In other words, the energy difference $(E_e - E_g)$ of the emitter is completely converted to photon energy $\hbar\omega$. The decay rate is obtained by summing over all available final states $|f\rangle$, where a final state is composed of the emitter in the ground state E_g with all different photon states, namely all different wave vectors (or directions) and polarizations. In modern Nanophotonics, Fermi's Golden rule is reformulated as [14–16]

$$\Gamma_{\text{rad}}(\mathbf{r}, \mathbf{o}_d, \omega) = \frac{\pi\omega d^2}{\hbar\epsilon_0} N_{\text{rad}}(\mathbf{r}, \mathbf{o}_d, \omega). \quad (1.2)$$

This expression factorizes into an emitter part depending on the magnitude of the dipole moment d , and a field part known as the projected local density of states (PLDOS) N_{rad} that is a property of the nanophotonic environment of the emitter, and that depends on the emitters' dipole orientation $\mathbf{o}_d$, position r , and the frequency ω .

1.3 Three-dimensional (3D) photonic band gap

By surrounding an emitter by a suitably tailored dielectric nanostructured environment, the vacuum fluctuations are controlled; the most radical control is

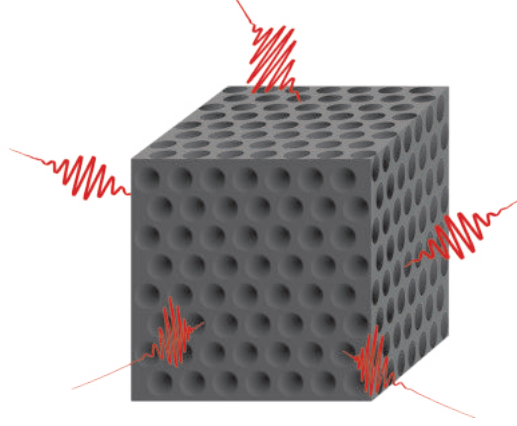


Figure 1.4: Cartoon of a finite three-dimensional (3D) photonic crystal embedded in free space. Since the crystal has a complete 3D photonic band gap, ubiquitous vacuum fluctuations incident on the crystal’s surface (shown as red wavelets) are forbidden from entering. Hence, an excited two-level quantum system (atom, ion, molecule, or quantum dot) inside the crystal cannot decay by spontaneously emitting a photon. Thus, the excited state becomes more and more stable.

offered by nanostructures with a so-called three-dimensional (3D) photonic band gap, as is studied in this thesis. Inside such special nanostructures, known as photonic crystals (see Section 1.5), all light waves with many photons, and hence all vacuum fluctuations with zero photons are forbidden by interference, since both are described by the same solutions of Maxwell’s equations for electromagnetic waves [17]. The vacuum fluctuations are then expelled from the nanostructure, as illustrated in Figure 1.4. Therefore an emitter inside such a 3D nanostructure experiences zero vacuum fluctuations, and the PLDOS vanishes ($N_{\text{rad}} = 0$). Hence, the emitter does not make the transition to the ground state anymore, no photon is emitted, the emission rate has vanished ($\Gamma_{\text{rad}} = 0$), spontaneous emission is said to be completely inhibited [18, 19], and the emitter’s excited state E_e becomes stabilized. If we then envision a further refinement of the nanostructure such that it allows just one mode of light [19], we achieve ultimate control over spontaneous emission, since our emitter is then considered to be a zero-threshold stimulated emitter or laser, an ultimate miniature emitter as discussed in Section 1.1.

Figure 1.5 shows how the relative LDOS changes with position and frequency of the emitters that are located inside a 3D photonic crystal. Nikolaev *et al.* [20] calculated dipoles positioned along characteristic axes in the unit cell of a 3D inverse opal photonic crystal made from titania (TiO_2). We show the LDOS projected on the dipole direction $e_d = [1, 1, 1]$ perpendicular to the dielectric-air interface for four different wavelengths $\lambda = 417, 624, 745, 1009$ nm. Converted to frequency, $\lambda = 1009$ nm corresponds to a frequency below all gaps (long-wavelength limit), $\lambda = 624, 745$ nm are in the range of first-order gaps, and $\lambda = 417$ nm is in the range of second-order gaps where eventually a complete 3D band

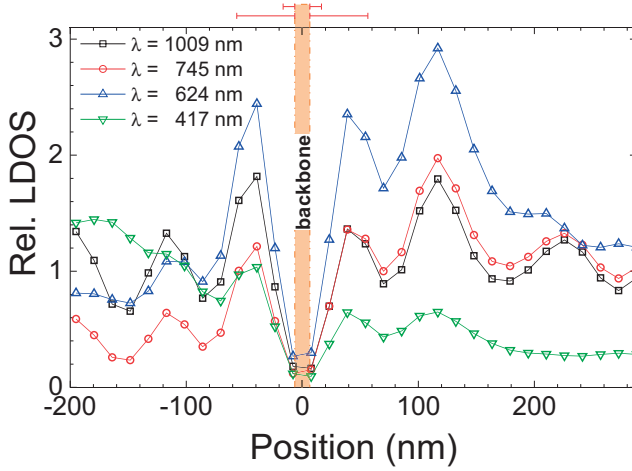


Figure 1.5: LDOS calculated for dipole emitters oriented along $e_d = [1, 1, 1]$ in a 3D cubic inverse opal from TiO_2 , as a function of position inside the photonic crystal. For different wavelengths $\lambda = 417, 624, 745, 1009$ nm the relative LDOS changes remarkably rapid. Above the top abscissa scale bars for 10 and 50 nm represent typical lengths of polymer brushes attached to the crystal backbone, to illustrate the main topic of this thesis namely, the precise control of quantum emitters inside 3D nanostructures. Figure adapted from Ref. [20].

gap develops (at higher photonic strength). The relative LDOS is significantly suppressed near the dielectric backbone ($r = 0$ nm) at all wavelengths, which is remarkable since the longest wavelength is below the gaps. Enhancements and inhibitions occur with fast changes on length scales of about 100 nm, which corresponds to $\lambda/10$ for the longest wavelength. If one could precisely control the position of a quantum emitter, its radiative rate would be strongly controlled from less than 0.1 (near the backbone) to nearly 3 (at 120 nm), corresponding to a whopping factor 25 or more. These observations motivates the research of this thesis, namely to place emitters at controlled positions inside photonic nanostructures.

1.4 Quantum dots

The kind of quantum emitters used and studied in this thesis are colloidal quantum dot (QD) nanocrystals. Quantum dots are semiconductor nanocrystals with a typical size (particle diameter) of several nanometer [21–23]. The advantages to use QDs as emitters instead of organic fluorescent molecules are that QDs do not blink or photo bleach after a longer period of time (after emitting about 10^8 photons). It is possible to synthesize quantum dot light sources with a desired frequency range since the emission frequency range is size-dependent [24–27]. The reason for this property is the quantum confinement that is explained below.

An image of a real sample consisting of lead sulfide quantum dots is shown in

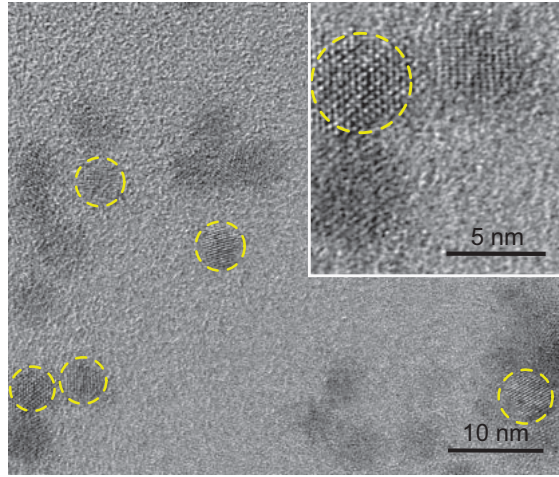


Figure 1.6: Transmission electron microscope (TEM) image of lead sulfide quantum dots with a PEG-NH₂ ligand. Individual quantum dots are circled in yellow for visualization. The scale bar for the overall image is 10 nm, for the inset 5 nm.

Figure 1.6. For the transmission electron microscope (TEM) image a suspension of quantum dots was placed on a TEM grid to achieve individual quantum dots on the surface. The quantum dots were coated by a polyethylene glycol-NH₂ ligand to make the quantum dots stable in water. Individual quantum dots are circled in yellow for visualization. In the inset (from the bottom left of the overall image) on the top right, individual atoms can be observed at a closer look. The average size of the quantum dots is around 5 nm.

How the the emission frequency range is determined by the quantum dot size, is visualized in Figure 1.7. The relation between the quantum dot size and its emission frequency is explained with the help of the particle-in-a-box model. On the left side in panel (a) a large quantum dot with a diameter of D is presented. The band diagram is shown below for the large quantum dot with its energy states E_{1e} , E_{2e} , and E_{3e} and the corresponding wave-functions. The smaller ΔD becomes, the more certain the location of the particle becomes, yet at the same time the momentum Δp becomes more uncertain as described by Heisenberg's uncertainty principle [28]. In panel (b) a smaller quantum dot with a diameter of D' is shown, where the energy levels are therefore further apart. Since the diameter of the quantum dot is smaller than twice the size of its exciton Bohr radius, the exciton is squeezed, which leads to quantum confinement. The exciton Bohr radius is the average distance between the hole in the valence band and the excited electron in the conduction band [29], as shown in Figure 1.8 (orange oval).

An electron is excited to the conduction band, leaving a hole in the valence band behind. The electron and hole attract each other because of attractive Coulomb interaction that forms a weakly bound exciton [30, 31]. After time τ the electron transitions back to the ground state into the valence band by emitting a photon. The energy levels, for the two quantum dots presented here,

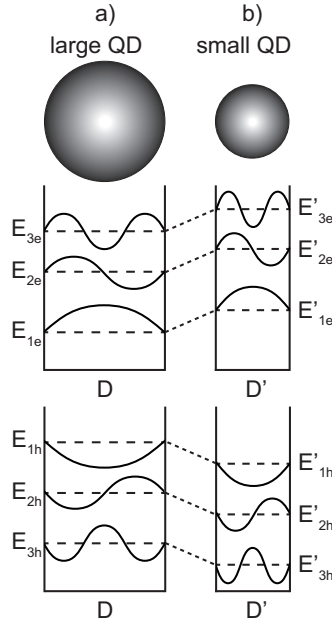


Figure 1.7: Particle-in-a-box model: a) a large particle with a diameter D sits in a box. b) a small particle sits in the same box as in a) with a smaller particle diameter D' . Only electromagnetic waves with an energy of 0 at the left and right side of the box are allowed. The first three discrete energy levels for the corresponding standing waves of the electron (E_e) are shown. The energy levels for the hole are shown as E_h .

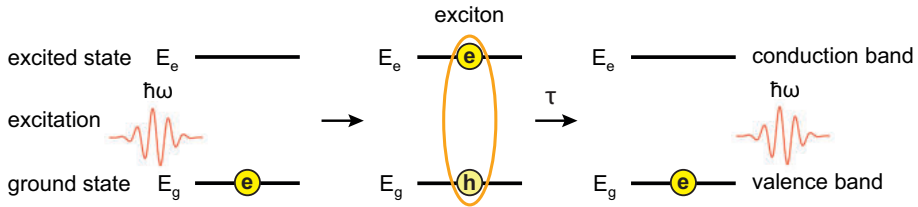


Figure 1.8: Schematic illustration of an ideal two level exciton: a) The electron is present in the valence band. The emitter is excited by a laser pulse, b) the electron and hole attract each other to form an exciton, c) the electron transitions back to its ground state by emitting a photon.

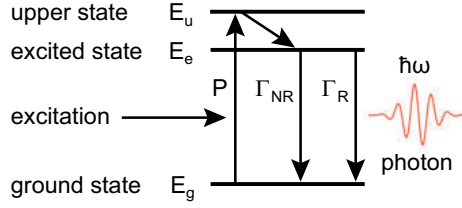


Figure 1.9: Three-level energy-scheme of an ensemble of emitters that are continuously excited, *e.g.*, by a CW laser. The incident laser light leads to some of the emitters being pumped by the rate P from the ground state (E_g) to the upper state (E_u), from where they relax very quickly to the excited state (E_e). Emitters in the excited state can decay via radiative- (Γ_R) or non-radiative (Γ_{NR}) decay channels.

differ, since the energy depends on the width of the box. That means the emission frequency can be predicted for every quantum dot depending on its crystal size.

Besides emission frequency range and lifetime τ , another quantum dot property is important, namely the quantum efficiency (QE). In addition to the spontaneous emission process, the radiative decay rate Γ_{rad} , real quantum emitters decay into non-radiative decay channels from loss processes. The non-radiative decay rate Γ_{nonrad} therefore adds up to the total decay rate Γ_{tot} which is equal to the sum of both processes:

$$\Gamma_{\text{tot}} = \Gamma_{\text{rad}} + \Gamma_{\text{nonrad}} \quad (1.3)$$

Figure 1.9 shows the different decay channels in a schematic.

Assuming that the non-radiative decay rate is lowering the intensity of the total emitted light, the quantum efficiency of an emitter is defined as:

$$QE = \frac{\Gamma_{\text{rad}}}{\Gamma_{\text{rad}} + \Gamma_{\text{nonrad}}} \quad (1.4)$$

The quantum dots used in this thesis are near-infrared (NIR) emitting quantum dots such that their emission frequency range is fitting to the 3D photonic band gap of the silicon photonic crystals studied. Candidates for this frequency range are lead sulfide (PbS) or lead selenide (PbSe) QDs [32]. Suitable dyes that emit in the NIR are rare and the ones that are available have low quantum efficiencies compared to the quantum dots [33]. Lead sulfide quantum dots were used in this thesis for several reasons. The dots are commercially available for a broad frequency range $\tilde{\nu} = 5900\text{--}12500 \text{ cm}^{-1}$ ($\lambda = 800\text{--}1695 \text{ nm}$). Furthermore they are available with different organic ligands, *e.g.* oleic acid (OA), glutathione (GSH), amine-PEGylated (PEG-NH₂), carboxyl-PEGylated (PEG-COOH), 3-mercaptopropionic acid (MPA), and have acceptable quantum efficiencies. In contrast to an ideal two-level exciton model, a real PbS quantum dot can have several energy levels for the hole state in the multi-level exciton model. As mentioned above, the band gap energy of the lead sulfide quantum dots was chosen to match with the 3D photonic band gap of the silicon photonic crystals to manipulate the decay rate of PbS nanocrystals *via* the local density of optical states.

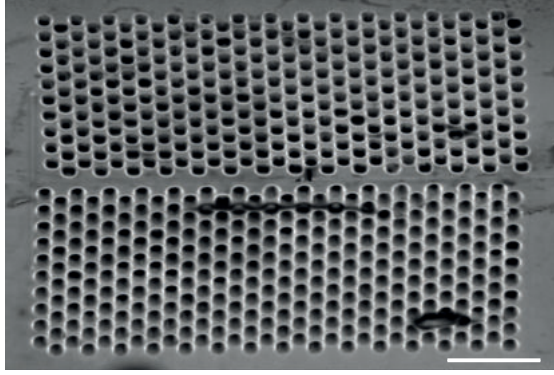


Figure 1.10: Scanning electron microscope (SEM) image of a 3D photonic crystal viewed from 45° on the edge of the silicon beam showing the XY (top) and the XZ surfaces (bottom); the scale bar indicates 2 μm . Image courtesy of Melissa Goodwin (COPS).

1.5 Photonic crystals

Three-dimensional (3D) functionalized nanostructures are drawing fast-growing attention for their advanced applications in nanophotonics [16, 34, 35], photovoltaics [36, 37], capacitors in electronics [38], gas sensing [39], materials for electrochemical energy conversion and storage [40], and batteries [41–44]. The functionalization of these nanostructures is the result of the infiltration of active nanoparticles, *e.g.*, fluorophores in nanophotonic light sources [45–47], antibodies for biochemical sensors of diseases, or quantum dots for photovoltaics [48, 49]. In most cases, the performance of the 3D-functionalized nanostructure depends on the precise positioning of the nanoparticles inside the 3D nanostructure, with nanometer precision. In nanophotonics, for instance, fluorescing nanoparticles should reside at positions where the local density of optical states is either maximal, in case of cavities or antennae, [5, 50, 51] or minimal in case of a photonic band gap [52, 53]. In biochemical detectors, antibodies should be positioned on the internal interfaces of the 3D substrate for maximum reactivity and selectivity [54].

Photonic crystals are ordered composite structures of at least two different materials with a periodicity on the order of the wavelength of light [19, 55]. Figure 1.10 shows a scanning electron microscope (SEM) image of a silicon photonic crystal fabricated by our group. Importantly the refractive index contrast of the neighboring materials has to be high. The obtained silicon-air photonic crystals used in this thesis are an example for a high index contrast. If visible light that has a broad frequency range is focused on these crystals Bragg diffraction occurs for wavelengths which are approximately equal to the periodicity of the lattice planes inside the structure. The Bragg condition is given by [56]

$$m\lambda = 2d\cos\theta \quad (1.5)$$

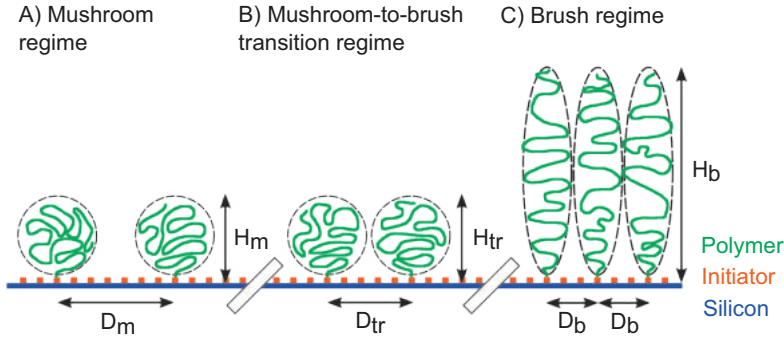


Figure 1.11: Effect of the grafting density to the polymer chains. At low grafting densities the polymer chains form mushroom- or pancake-like structures (A). With increasing density the polymer chains are more close to each other (B). At high grafting densities the polymer chains stretch away from the surface and the height H_b of the polymer layer increases (C).

where λ is the Bragg diffracted wavelength, m an integer that corresponds to the order of the diffraction, d the distance between the lattice planes and θ the angle of the propagating light wave with respect to the crystal planes.

Famous examples for photonic crystals appearing in nature are opals [57] and butterfly wings [58, 59]. The change in color depending on the angle appears because of the physics mentioned above.

1.6 Polymer brushes

This thesis reports the strategy to control the position of nanoparticles inside 3D silicon photonic crystals by covalently attaching nanoparticles, *e.g.* quantum dots, to different kinds of surface-grafted polymer chains. A polymer chain is an organic macromolecule that is composed of many smaller repeating sub-units called monomers [60]. The pore surface of the photonic crystal can be modified by either grafting polymer chains from an active surface so-called grafting-from [61] or the covalent attachment of presynthesized functional polymer chains to the surface [62]. Polymer brushes are a frequently employed and special form of surface-bound polymer grafts that possess chains in a stretched conformation in good solvents due to molecular crowding. This crowding dominates the structure of the brushes and thus the properties of the grafted layer if the attachment distance between neighboring chains substantially reaches the unperturbed chain diameter in good solvents [63]. The most important advantage of these densely packaged macromolecules is the maximization of functional groups per unit area and thus the possibility to further functionalize the polymer layer by covalently attach nanoparticles.

Figure 1.11 shows the effect of the grafting density on the polymer chains. At low grafting density the distance D_m between individual polymer chains is high

and the collapsed macromolecules form mushroom-like structures on the surface (A) [64]. With increasing chain density the distance D_{tr} within the mushroom-to-brush transition regime between the macromolecules decreases (B). The height of the polymer layer H_{tr} does not change significantly compare to the height H_m within the mushroom regime. Additionally the conformation of the polymer chains is similar in both regimes. Once the density is high enough, the individual polymer chains start to stretch away from the surface forming polymer brushes (C). The height H_b of the polymer layer significantly increases. When the spacing between individual chains becomes smaller than their radius of gyration, the molecules start to stretch away from the surface as a result of the increased osmotic pressure or to avoid contacts [65].

Surface-initiated polymerizations (SIPs) are used in this thesis and are well understood polymerization reactions [66]. For the functionalization of the nanopores of the silicon photonic crystals a highly reliable SIP method is crucial. Surface-initiated atom transfer radical polymerization (SI-ATRP) that is a special form of a "living" polymerization, is a good candidate. This polymerization technique was first based on bulk and solution ATRP which was developed by Sawamoto *et al.* [67] and Matyjaszewski *et al.* [68]. Advantages of this technique are the mild reaction conditions, compatibility with a wide variety of monomers, and the fine control over chain length and the end group functionalities.

1.7 Characterization of nanostructures

What is a suitable diagnostic tool to probe whether polymer brushes have been synthesized *inside* a monolithic 3D nanostructure and whether quantum dots are positioned inside? Atomic force microscopy (AFM) has a nanometer resolution on surfaces, but the typical dimensions of an AFM tip precludes to sense inside the nanopores typical of our 3D structures [69]. Scanning tunneling microscopy (STM) has a nanometer resolution on surfaces, but the distance of the STM tip to any conducting surface is way too far [69]. In ellipsometry the lateral information is averaged over the typical millimeter extent of the incident beam, moreover there is no element specificity. X-ray photo-electron spectroscopy (XPS) is element specific, since characteristic X-rays emitted by different elements are distinguished. Unfortunately, however, the spatial resolution is in the 10s of micrometer range and the depth penetration is only a few nanometer, which is much too coarse for our purpose.

All techniques that were mentioned so far are used for the characterization of surfaces. To visualize 3D nanostructures and their elemental composition, a known technique in nanofabrication is the combination of scanning electron microscopy with micro-machining or focused ion beam milling, and energy dispersive X-ray spectroscopy (EDX) [70, 71]. Unfortunately, FIB-SEM-EDX is destructive, irreversible, and the sensitivity of EDX is not sufficient.

Compared to all other techniques, X-ray techniques offer high penetration and high resolution. The goal to use a nondestructive diagnostic tool is shown in Figure 1.12. Small-angle X-ray scattering (SAXS) for example is employed to

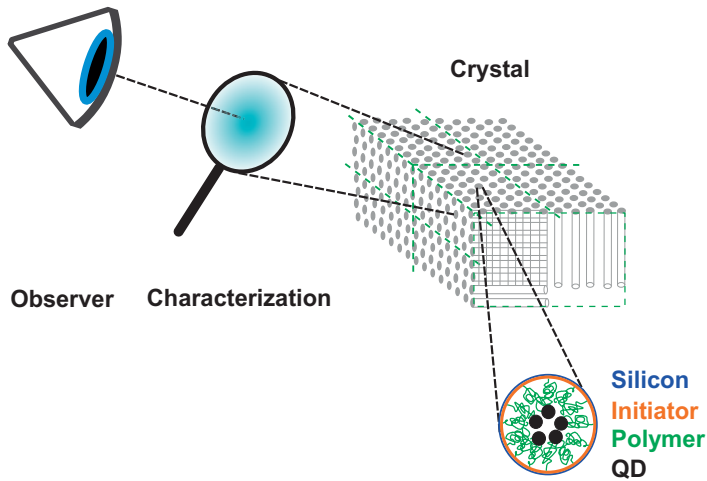


Figure 1.12: The ideal diagnostic tool to probe a complex nanostructure. An observer is looking at a sample that is analyzed by the characterization method. Detailed 3D information is retrieved in a nondestructive manner.

study 3D nanoparticle arrays. The disadvantage of SAXS is that this method is not straightforward to be used for the characterization of 3D nanostructures since it naturally operates in reciprocal space [72, 73]. With the use of an anomalous scattering approach, even element specificity can be obtained for two different elements. The technique is called anomalous small-angle X-ray scattering (ASAXS) [74]. Since we had to characterize more than 6 different elements, this techniques would not be suitable. Therefore, we decided to study our structures by means of X-ray fluorescence tomography using a synchrotron source, since this method allows for nanometer resolution in 3D, it is nondestructive, and element specific [75–77].

1.8 Outline of this thesis

In this thesis the primary goal is to control the spatial locations of quantum dots that are placed into a 3D photonic crystal and to determine the average decay rates of the nanoemitters. The experimental data on silicon-surface chemistry is presented (Chapters 2 and 3) that shows a strategy to control a polymer layer thickness in the range of 10s of nanometer. These polymer layers were used to attach quantum dots to the polymer chains to control their position and density on the surface. Furthermore, optical measurements on quantum dot suspensions (Chapter 4), and quantum dots positioned on flat polymer layers and inside 3D photonic crystals (Chapter 7) are presented. A detailed cleaning procedure of silicon photonic crystal samples is shown in a supporting chapter (Chapter 5). The first time ever X-ray fluorescence tomography measurements on periodic nanostructures with embedded near-infrared emitting quantum dots

are presented as a highlight of this thesis (Chapter 6).

The starting experimental chapter of this thesis will deal with the aim to control the layer thickness of poly(*N*-isopropylacrylamide) (PNIPAM) brushes on flat silicon substrates. The synthesis and characterization of PNIPAM brushes are reported in detail. For this chapter the goal is to show that a control over the polymer layer thickness can be achieved by varying the ratios of activating- and deactivating copper catalyst species.

In Chapter 3 the covalent attachment of lead sulfide quantum dots to poly(glycidyl methacrylate) brushes is presented. Here the aim is to prove that the layer thickness can be controlled with the polymerization time to obtain samples with different thicknesses. The particle density on the polymer brush layers is varied with the concentration of the quantum dot suspension. In this chapter fluorescence microscopy is discussed as a characterization method for the particle density of visible quantum dots.

Chapter 4 describes the optical measurements on lead sulfide quantum dot suspensions. Spectra and time-resolved emission were measured on lead sulfide quantum dots suspended in chloroform, toluene and water, depending on the organic ligand shielding the nanocrystals. The goal of this chapter is to present characteristic data for different types of lead sulfide quantum dots. The collected data of quantum dot suspensions will help to understand the upcoming measurements of quantum dots placed into 3D silicon photonic band gap crystals.

A supporting chapter of this thesis is Chapter 5. To ensure a successful surface chemistry as presented in Chapters 2 and 3, an accurate cleaning procedure for the silicon photonic crystals had to be developed in the cleanroom. Fluorocarbons present on the silicon surface after the deep reactive ion etching procedure for the photonic crystals would prevent an elaborate silane surface chemistry followed by atom-transfer radical polymerization. It is studied whether harsh wet chemical treatments and the oxidation at high temperatures in a furnace can lead to clean silicon nanostructures.

In the experiments presented in Chapter 6 element-characteristic fluorescence was measured via X-ray fluorescence tomography at the synchrotron in Grenoble (European Synchrotron Radiation Facility, ESRF). The samples studied in this chapter were fabricated using the knowledge obtained from the experimental data of Chapters 2, 3 and 5. Chapter 6 presents a detailed discussion whether the fabrication strategy to control the spatial location of quantum dots by polymer brushes was successful.

Chapter 7 presents the experimental data obtained from optical measurements on quantum dots attached to polymer brushes for flat silicon, 2D and 3D photonic crystals. Building on the knowledge obtained from experiments in Chapter 4, emission spectra and time-resolved lifetime traces are presented. The aim of this chapter is to discuss the effect of a photonic band gap that possibly influences the properties of the nanoemitters.

CHAPTER 2

Controlled sub-ten-nanometer poly(*N*-isopropylacrylamide) layers grafted from silicon by atom transfer radical polymerization

Surface-initiated atom transfer radical polymerization (SI-ATRP) was used to graft poly(*N*-isopropylacrylamide) (PNIPAM) brush layers with a controllable thickness in the 10-nm range from silicon substrates. The rate of polymerization of *N*-isopropylacrylamide was tuned by the $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio between the deactivating and activating species. The polymer layer thickness was characterized by atomic force microscopy (AFM) and ellipsometry. PNIPAM layers with a dry thickness between 5.5 and 16 nm were obtained. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) confirmed that the chemical structure is PNIPAM. Analysis of the AFM data showed that our procedure leads to polymer grafts in the “mushroom-to-brush” transition regime.

2.1 Introduction

Polymer grafts attached to various substrates have been used with great success to engineer both surface and interfacial properties of the material to which they are anchored. Brushes, a frequently employed form of surface bound polymer grafts, possess chains in a stretched conformation in good solvents due to molecular crowding. This crowding dominates the structure and thus the properties of the grafted layer if the attachment distance between neighboring chains substantially reaches the unperturbed chain diameter in good solvents [63]. Polymer brushes have found use in a broad range of applications [78–83], such as altering the wetting behavior of surfaces [84], forming ion transport barriers [85, 86], fabricating protein microarrays [87], in antibody immobilization [88], in tissue engineering [89], and for manipulating nanoparticles [90]. Our interest is to covalently attach quantum dot nanocrystals to the ends of polymer brushes, to control the position of such emitters in the 10-nm range so as to control their spontaneous emission and energy transfer rates [16, 20, 91]. Since silicon yields powerful nanophotonic

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structures, even planar, we choose it as a substrate. Since position tunability is a desirable feature, we choose poly(*N*-isopropylacrylamide) (PNIPAM) since it is a stimulus-responsive polymer material that allows to tune its thickness by swelling in a suitable solvent or by temperature [92, 93].

The preparation of relatively smooth and homogeneous polymer brush layers by surface-initiated atom transfer radical polymerization (SI-ATRP) is known to be well-controlled [94]. SI-ATRP is a versatile method to tune the layer thickness with a narrow distribution in molar mass of the grafted chains [67, 68, 81, 95–100]. However, grafting thin PNIPAM brushes from a surface is challenging due to the fast polymerization rate of NIPAM in aqueous media [101]. Reproducible procedures for obtaining brush layers of PNIPAM with thicknesses in the sub-10-nm range (hereinafter ultrathin brush layers) in the dry state are sparse for dense ATRP-initiator concentrations on the surface.

One possibility to achieve a better control is provided by slowing down the polymerization rates. The rate of ATRP essentially depends on the rate constant of propagation of the polymerization, on the concentrations of the monomer and the growing radicals. In ATRP, the radical concentration depends on the equilibrium constant of the reaction, and on the concentrations of the dormant species, activators (*e.g.*, Cu(I)), and deactivators (*e.g.*, Cu(II)). For example Zhang, *et al.*, demonstrated experimentally that the $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio, tuned by the addition of deactivating Cu(II) to the initial polymerization reaction mixture, has strong effects on the kinetics of ATRP [102]. In parallel with slowing down the polymerization rate, the addition of deactivating Cu(II) to the ATRP reaction mixture also improves the control over the molar mass and the polydispersity [103]. To our knowledge, tuning the $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio has so far not been used to obtain PNIPAM layers with thicknesses in the 10-nm range. One of the challenges to control the ATRP of acrylamide monomers like NIPAM is caused by catalyst inactivation [104–106]. Due to complexation of copper by the growing polymer chain and the monomer, and due to the displacement of the terminal halogen atom by the nucleophilic amide group, the system can become deactivated. Kizhakkedathu, *et al.*, polymerized PNIPAM with a well-defined thickness from polystyrene latex particles [107]. Fulghum, *et al.*, reported the polymerization of ultrathin PNIPAM brushes on top of a membrane surface [108]. Alem, *et al.*, reported the growth of PNIPAM brushes from nanopore walls of poly(ethyleneterephthalate) membranes [109]. Malham and Bureau reported a procedure to graft PNIPAM layers by reducing the initial ATRP initiator coverage [110]. For a 10 nm thin PNIPAM layer they reported a low grafting density of 0.02 chains per nm². Cimen and Caykara presented oligoPNIPAM brushes with -OH and -COOH end-groups [111]. Pomorska, *et al.*, showed that the layer thickness can be influenced by the solvent composition between water and methanol [112]. However, a precise control over the layer thickness in the 10-nm range was not provided.

Here we present the fabrication of ultrathin PNIPAM layers with thicknesses in the 10 nm range grafted from silicon substrates via SI-ATRP by varying the $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio. The initiator density on the substrates was kept constant during the procedures. We aimed for a high initiator density to graft dense

polymer chains from the substrate. The polymer brush thickness was controlled by the deactivating copper(II) species to slow down the polymerization rate. Our approach leads to smooth and homogeneous ultrathin PNIPAM polymer layers as confirmed by ellipsometry, time-of-flight secondary ion mass spectrometry (ToF-SIMS), and atomic force microscopy (AFM).

2.2 Materials and methods

2.2.1 Materials

N-Isopropylacrylamide (NIPAM, 97%, Sigma-Aldrich) was recrystallized from a toluene/hexane mixture (50%, v/v) and dried under vacuum before use. Copper(I) bromide (CuBr, Sigma-Aldrich, 98%) was purified by stirring in glacial acetic acid, filtering and washing with ethanol three times. The catalyst was dried under vacuum at room temperature for 48 h. Copper(II) bromide (CuBr₂, Sigma-Aldrich, ≥99%), methanol (Biosolve, 99.8%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDTA, Acros Organics, 98%), 2-bromo-2-methylpropionic acid allyl ester (Sigma-Aldrich, 98%), hexachloroplatinic acid (Sigma-Aldrich, 99.9%) and dimethylchlorosilane (Sigma-Aldrich, 98%) were used as received. Millipore Milli-Q grade (18 MΩcm) water was used in the experiments.

2.2.2 ATRP initiator synthesis and characterization

Chemical synthesis

The ATRP initiator was synthesized following Ramakrishnan, *et al.* [113]. 2-Bromo-2-methylpropionic acid allyl ester (4 mL) was mixed with an excess of freshly distilled dimethylchlorosilane (8 mL). A few granules of hexachloroplatinic acid were added and the mixture was stirred for 48 h at room temperature under argon. The excess of chlorosilane was removed by first flushing the reaction flask with nitrogen for 24 h. Afterwards the remaining chlorosilane was removed under reduced pressure. The slightly yellowish oil was quickly filtered over small amounts of anhydrous sodium sulfate to remove the residual catalyst.

Nuclear magnetic resonance (NMR)

¹H NMR (CDCl₃, 400 MHz): δ = 4.09 ppm (t, 2H, -CH₂O-), 1.90 (s, 6H, -Si-CH₃-), 1.61-1.69 (m, 2H, -CH₂-), 0.51-0.56 (m, 2H, -Si-CH₂-), 0.04 (s, 6H, -Si-(CH₃)₂-).

¹³C NMR (CDCl₃, 400 MHz): δ = 171.85 ppm (C=O), 68.51 (CH₂-O), 56.19 (C_{ter}), 30.98 (C-CH₃), 22.59 (CH₂-CH₂), 14.20 (Si-CH₂), 0.45 (Si-CH₃).

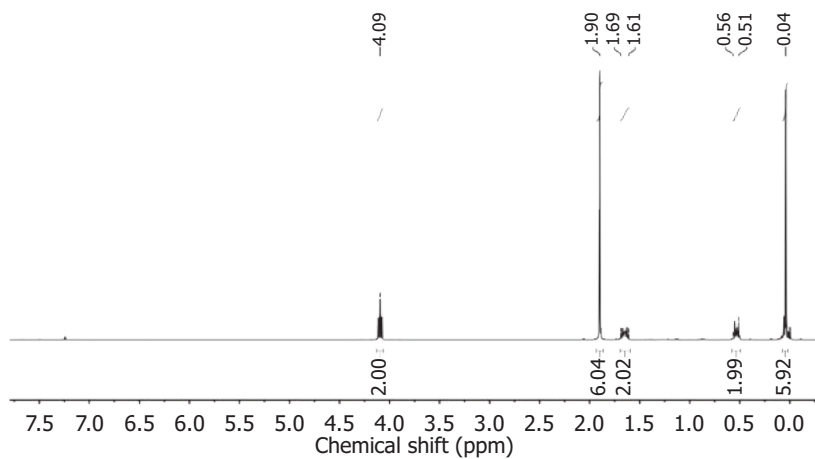


Figure 2.1: ^1H NMR spectrum of the ATRP initiator.

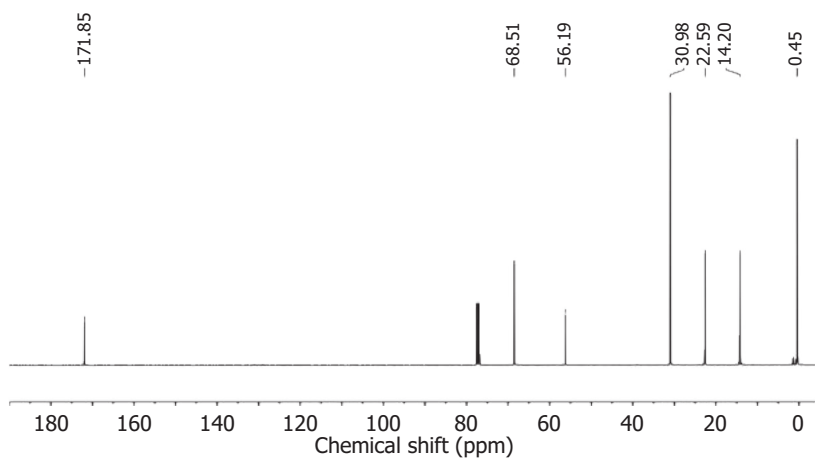


Figure 2.2: ^{13}C NMR spectrum of the ATRP initiator.

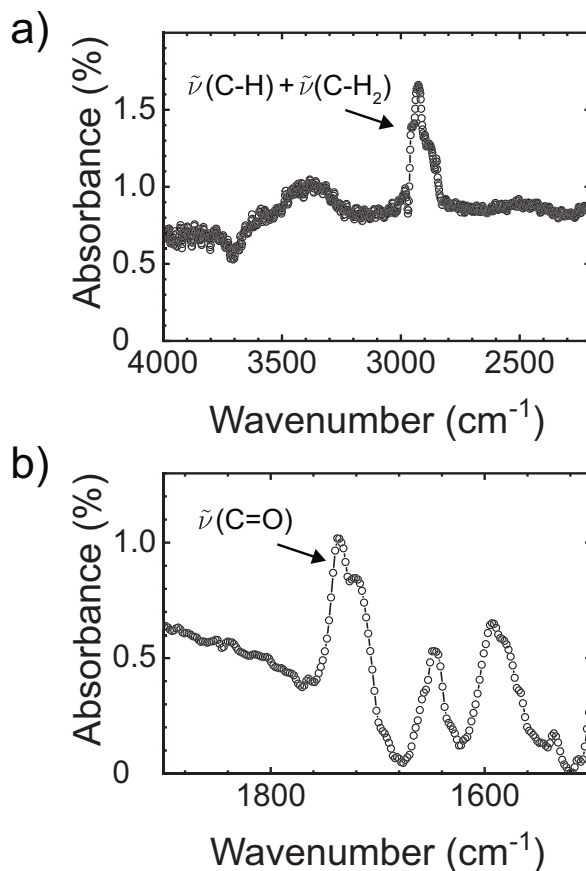


Figure 2.3: FT-IR spectra of the ATRP initiator for the wavenumber range a) 2000–4000 cm^{-1} with $\tilde{\nu}(\text{C-H})$ and $\tilde{\nu}(\text{C-H}_2)$ stretch motions and b) 1500–1900 cm^{-1} with the $\tilde{\nu}(\text{C=O})$ stretch motion.

Attenuated total reflection infrared spectroscopy (ATR-IR)

The ATRP initiator was analyzed using attenuated total reflection (ATR) in the infrared (IR). An ATR accessory was implemented in a FT-IR instrument (Vertex 70v, Bruker) to increase the signal for analyzing the monolayer. To illustrate the characteristic bonds within the initiator molecule, the structure is shown in Figure 2.4.

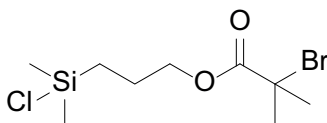


Figure 2.4: Chemical structure of the ATRP initiator.

The IR-spectrum shows the $\tilde{\nu}(\text{C}=\text{O})$ stretching vibration around 1737 cm^{-1} and the $\tilde{\nu}(\text{C-H})$ stretching vibrations between 2927 and 2851 cm^{-1} (Figure 2.3).

2.2.3 Chemical synthesis of PNIPAM polymer brushes

ATRP initiator vapor-phase deposition: Silicon substrates were cut into pieces of $1.2 \times 1.2\text{ cm}$, cleaned with piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, 3:1 v/v) for 30 min, and extensively rinsed with water and ethanol. *Caution: Piranha solution reacts violently with many organic materials and should be handled with great care!* The substrates were dried in a nitrogen stream. ATRP initiator ($30\text{ }\mu\text{L}$) was placed onto a small plastic petri dish at the bottom of a desiccator and the previously cleaned silicon substrates were placed around it. The desiccator was evacuated by a rotary vane pump for 10 min. Vapor-deposition was allowed to proceed for 16 h. Afterwards the samples were sonicated in toluene for 1 min, washed with ethanol and water, and dried in a nitrogen stream.

ATRP procedure of PNIPAM: NIPAM (6 g, 53 mmol) monomer and PMDTA ($165.9\text{ }\mu\text{L}$, 0.79 mmol) were added to a mixture of water (10 mL) and methanol (10 mL). The solution was purged with argon for 30 min under continuous stirring. The $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio was varied between 7% and 10% in four steps. As an example the $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio of 10% is given. Cu(I)Br (34.5 mg, 0.24 mmol) and Cu(II)Br_2 (5.4 mg, 0.024 mmol) were added to another flask and flushed with argon for 15 min. The molar ratio of the reactants was 100:1.5:0.5:0.05 (NIPAM/PMDTA/ $\text{CuBr}/\text{CuBr}_2$). The monomer solution was transferred by a previously flushed syringe to the catalyst flask. The resulting polymerization solution was stirred for an additional 30 min under argon while stirring. Afterwards the solution was transferred by a previously flushed syringe to the reaction flasks containing the substrates. The polymerization was allowed to proceed for 30 min. After the polymerization was done the substrates were cleaned extensively with Milli-Q water and with ethanol to remove non-reacted monomer, metal-complex, and remaining catalyst residues. The samples were dried in a nitrogen stream to obtain the silicon substrates with the thin poly(*N*-isopropylacrylamide) polymer brush film.

Figure 2.5(a) shows the polymerization solution of NIPAM with the copper-PMDTA-complex in water/methanol mixture. The typical teal color of the solution is caused by the transition metal complex of copper with PMDTA. The more copper(II) bromide is present in the solution the more blueish the polymerization solution becomes. The result is a clear polymerization solution since all compounds dissolve well in the solvent mixture. An image of a silicon substrate after the polymerization is shown in Figure 2.5(b). On the left side a clean silicon

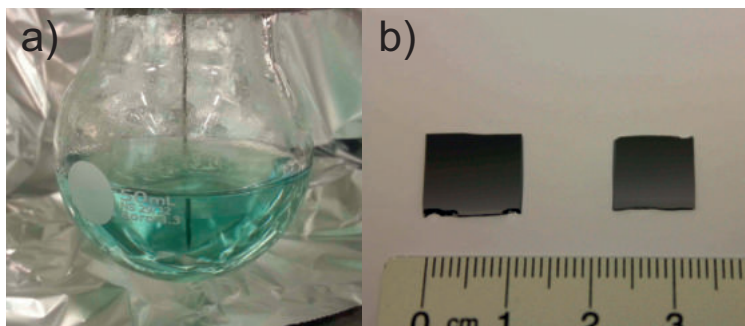


Figure 2.5: (a) Polymerization solution of NIPAM with the copper-PMDTA-complex in water methanol mixture. The monomer, copper(I) bromide, copper(II) bromide and PMDTA have completely dissolved to form a homogenous teal-colored solution. The solution is purged by a needle to remove oxygen; (b) Image of the silicon substrates before and after the polymerization. The left substrate is a clean silicon wafer without a polymer layer. The right substrate is has a layer of PNIPAM brush made by ATRP. The thin polymer layer is not visible by the naked eye, since the polymer thickness is only about 10 nm thick.

wafer piece without a polymer layer after piranha cleaning is shown. On the right hand side a substrate with a layer of PNIPAM brush after the polymerization is presented. By eye one cannot see a clear difference compared to the clean substrate. The polymer layer thickness is only about 10 nm thick, which is not visible by the naked eye since the thickness is much less than visible wavelength.

Ellipsometry

The dry thickness of a surface-grafted PNIPAM film was determined by a variable-angle spectroscopic ellipsometer (VASE ellipsometer base model, LOT Oriel GmbH, Darmstadt, Germany) at three different angles of incidence (65° , 70° , and 75°) at room temperature. The thickness was determined via the analysis of a three-layer (Si/SiO₂/PNIPAM) model with known thicknesses of the Si and SiO₂ layers and known refractive indices of the Si and SiO₂ layers (software WVASE32, LOT Oriel GmbH, Darmstadt, Germany). It was assumed that the polymer has a refractive index of 1.47 [114].

Time-of-flight secondary ion mass spectrometry

The ToF-SIMS measurements were performed on a ToF-SIMS IV-100 (ION-TOF GmbH, Münster, Germany) located at the University of Siegen that was equipped with a bismuth liquid metal ion gun (LMIG) kindly made available by Dr. Lars Birlenbach. A Bi₃⁺ primary beam at 25 keV was used in a high-current bunched mode to measure spectra for positively charged fragments with a pulse width of 0.15 ns. The target current was set to 0.2 pA. All spectra were taken from an area of 100×100 (128 × 128 pixels). Positive ion spectra were internally mass calibrated using CH₃⁺, C₂H₅⁺ and C₃H₇⁺ peaks.

Atomic force microscopy

AFM measurements were performed in tapping (dry brush thickness and roughness) and contact (wet brush thickness) modes using the Multimode 8 AFM retrofitted with the NanoScope V controller and the JV vertical engage scanner (Bruker, Santa Barbara, CA, USA). In tapping mode, a commercially available high-frequency (320 kHz) silicon cantilevers (model NCH, NanoWorld, Switzerland) with a nominal spring constant of 42 N/m and a nominal tip radius of 8 nm (shape of polygon based pyramid) were used. The scanning was performed at a scan rate of 0.5 Hz with the ratio of set point amplitude to free oscillation amplitude of about 0.75.

For contact mode, custom-made colloidal probes were manufactured using a soft cantilever (TL-CONT, Nanosensors, Switzerland; nominal spring constant of 0.2 N/m) and polystyrene (PS) bead (Duke Standards 4205A, Thermo Scientific, USA; diameter of 5 μm), to induce high contact area with the brush, and thus to reduce the applied contact pressure. The colloidal probes preparation contained the following steps: (1) PS particles were diluted in water and drop-coated on a freshly cleaved mica surface, then dried with nitrogen; (2) individual beads were attracted from mica by a tungsten wire (World Precision Instruments, Inc.) controlled by a home-made micromanipulator under an optical microscope; (3) the tungsten wire was chemically etched at 30 V in 1 M KOH water solution until the end-diameter was of about 10-15 μm in order to transfer individual colloids; (4) the wire was immersed in ethanol and dried under nitrogen to induce a proper wire-colloid capillary adhesion; (5) the beads were adhered using a UV-cured glue (Optical Adhesive 81, Norland Products, Inc.) to the end of the cantilever and photocured using high intensity UV lamp (Hamamatsu LC8, type 02A) for 3 minutes in air. The quality of the colloidal probes was carefully checked by optical and scanning electron microscopy imaging.

The contact mode imaging with colloidal probes was conducted in water, which was injected via a syringe to the liquid cell; the system was alone to attain equilibrium for 20 minutes. The cantilever spring constant was determined in water by the thermal tuning method [115, 116]. The imaging was performed at a scan rate of 0.3 Hz with a load force of 1.6 nN, which corresponds to the lowest possible force value that still allowed us to obtain stable images with a clear step height profile in the brush. All images, either for tapping or contact mode, were collected at a temperature of 21 $^{\circ}\text{C}$. The temperature was strictly controlled; fluctuations were smaller than 0.2 $^{\circ}\text{C}$. Image processing and data analysis were conducted with the NanoScope (ver. 8.15) and the NanoScope Analysis software (ver. 1.7), respectively. To quantify the average height variation, a step height analysis was performed.

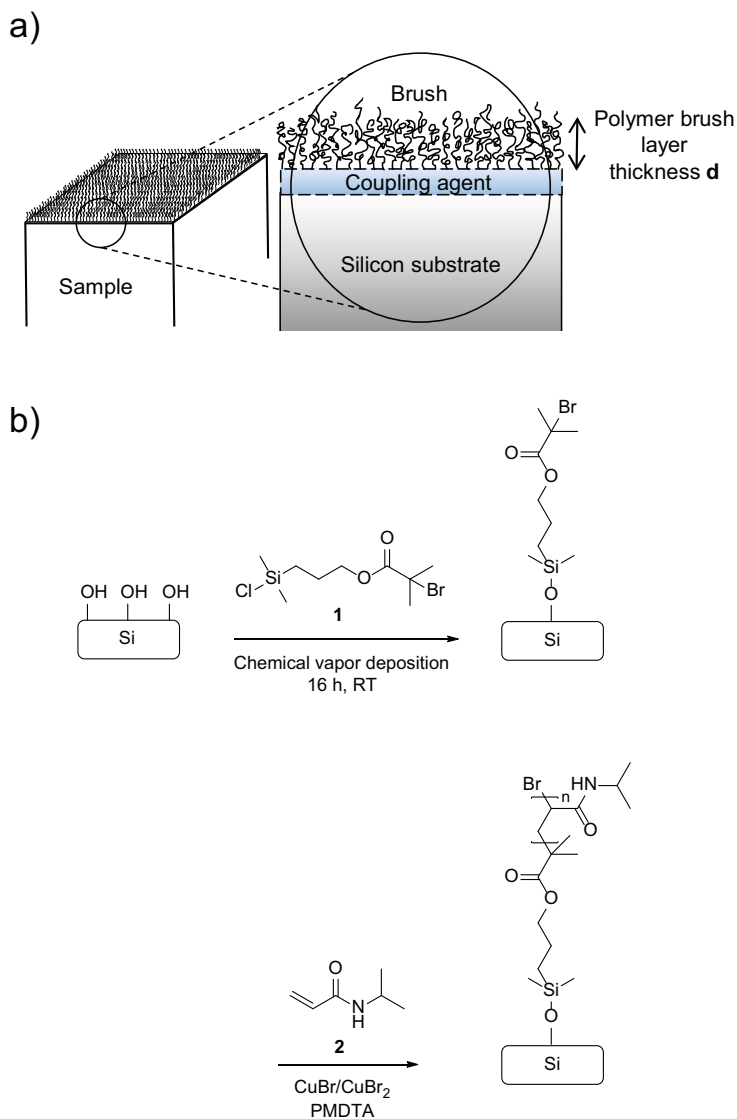
2.3 Results and discussion

2.3.1 Sample fabrication

A typical sample was fabricated in three main steps. The chemical process followed in this study is summarized in Figure 2.6. First, silicon substrates were cut

into pieces of 1.2 x 1.2 cm, cleaned with a Piranha solution, extensively rinsed with water and ethanol, and dried in a nitrogen stream. In the second step, the coupling agent 3-(chlorodimethylsilyl)propyl 2-bromo-2-methylpropionate **1** was reacted with the cleaned silicon substrates by chemical vapor-deposition (CVD). The initiator coverage was kept constant in this study. Thirdly, the resulting highly hydrophobic surface was used to graft short PNIPAM chains from the initiator molecules. The polymerization solution consisted of the monomer NIPAM **2**, the ligand and the catalyst. Cu(I) and Cu(II) bromide were used to form transition-metal complexes with the ligand *N,N,N',N',N''*-pentamethyldiethylene-triamine (PMDTA). The characteristic color of the polymerization solution can be seen in Figure 2.5(a). Cu(II) bromide was added to slow down the polymerization rate. The molar ratio of $[\text{Cu(II)Br}_2]/[\text{Cu(I)Br}]$ was varied between 7% and 10%. Below a $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio of 7% we observed that the polymerization is too fast and thus not reproducible. Beyond a $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio of 10% we observed an increasing difficulty to dissolve the Cu(II) bromide. Four different polymerization batches were made to study the effect of Cu(II) on the reaction kinetics. For each batch three samples were synthesized and characterized.

Following completion of the polymerization, the samples were extensively cleaned with Milli-Q water and with ethanol to remove non-reacted monomer, metal-complex, and remaining catalyst residues. The samples were finally dried in a nitrogen stream to obtain silicon substrates with thin poly(*N*-isopropylacrylamide) polymer brush films. The molecular characterization of polymer brush surfaces remains a challenging scientific task [117]. To characterize the PNIPAM layers we employed time-of-flight secondary ion mass spectrometry, atomic force microscopy, and ellipsometry. ToF-SIMS was used to analyze the chemical composition of the polymer brush film. AFM was used to study the morphology and the thickness of the polymer brush on the silicon substrate in both dry and wet states. Furthermore AFM measurements in water were performed to derive the grafting density of the brushes. Ellipsometry was used to analyze the polymer layer thickness and to provide complementary information to AFM.



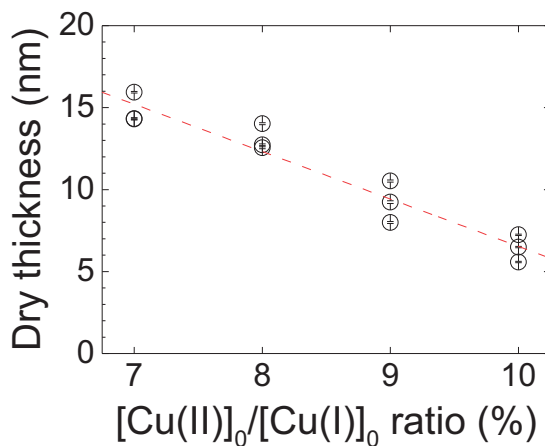


Figure 2.7: Brush thickness d_e of the PNIPAM layers, determined from ellipsometry, as a function of the $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio for a polymerization time of 30 minutes in water/methanol (50%, v/v). Black circles present the average thickness for one substrate. The dashed red line is a guide to the eye. With increasing $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio the polymerization rate of grafting PNIPAM chains from the Si surface decreases.

2.3.2 Effect of $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio on brush thickness

Figure 2.7 shows the averaged dry polymer thickness d_e obtained as a function of the $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio. Table 2.1 presents the dry thickness for each substrate measured by ellipsometry. Since our procedure leads to ultrathin brush layers, ellipsometry reaches its limits to obtain a reliable value for the layer thickness [118]. To confirm the thickness determined by ellipsometry we studied our samples with AFM to derive the polymer layer thickness with a different analytical method. Since both methods are based on different physics and have a completely different error margin, a direct comparison should be interpreted as an indication only. Figure 2.7 shows a decreasing linear trend with increasing $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio. Thus, these data reveal that the $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio controls the thickness of the grafted layer. In the ATRP reaction Cu(I) becomes oxidized to Cu(II) by extracting a halide atom from the dormant species. Adding more Cu(II) halide shifts the equilibrium towards the dormant state, by enhancing the concentration of alkyl halides P_nX , thus slowing down the ATRP reaction rate and leading to a thinner layer. The thickness range accessible by the procedure described here is limited by the solubility of Cu(II) bromide in the water/methanol mixture, down to $d \approx 6$ nm.

2.3.3 Chemical composition

The chemical composition of the polymer films was investigated by ToF-SIMS, which is a surface-sensitive method to characterize thin films, where the small primary ion beam removes a thin layer of the surface [119]. Several papers

Table 2.1: Dry thickness d_e of PNIPAM brushes measured by ellipsometry

thickness (nm) 7% [Cu(II)] ₀ /[Cu(I)] ₀	thickness (nm) 8% [Cu(II)] ₀ /[Cu(I)] ₀	thickness (nm) 9% [Cu(II)] ₀ /[Cu(I)] ₀	thickness (nm) 10% [Cu(II)] ₀ /[Cu(I)] ₀
14.30 ± 0.05	12.55 ± 0.06	7.99 ± 0.06	5.58 ± 0.04
14.33 ± 0.05	12.74 ± 0.06	10.52 ± 0.06	6.49 ± 0.04
15.94 ± 0.05	14.02 ± 0.06	9.24 ± 0.08	7.24 ± 0.04

reported the use of ToF-SIMS to characterize thin films [120–122]. The analysis of the chemical composition via ToF-SIMS was performed as the method provides information on the molecular structure of a thin film in a very sensitive manner. The polymer layers were directly measured at the substrate to which they are anchored.

In addition, ToF-SIMS offers the possibility to obtain an intensity “map” for different fragments. We use the term map to define an area scan on the substrate to verify the compositional homogeneity. With the help of the intensity map it is possible to assess whether the fragments are formed homogeneously across the whole scan area; some representative examples are shown in the Supporting Information in Ref. [123] (Figures S6-S9). These data show that the layers were homogeneous across the substrate.

From the ToF-SIMS measurements the positively charged fragments formed in the surface ionization process were analyzed. The measured counts per fragment as a function of mass are shown in Figure 2.8(a). To clarify the important mass peaks, we added the corresponding masses of the fragments to the plot. We observed six main fragment masses besides lower intensity counts for impurities, or for other fragments formed during the measurement. Starting from the lowest fragment mass, distinct peaks were observed at $m/z = 27, 43, 55, 58, 72$, and 114 . Since similar mass patterns have been reported in the literature for PNIPAM, we used these results as a starting point to obtain peak assignment for PNIPAM grafts studied here [124–128]. We propose the assignment of the corresponding chemical structures of these most important fragments in Figure 2.8(b). The characteristic peaks observed at $43\ m/z$ ($C_3H_7^+$, isopropyl) and at $114\ m/z$ correspond to one monomer unit of NIPAM. The other measured fragments are in good agreement with the calculated masses, apparently no trace of the initiator could be detected. In Figure 2.8(c) we plot the counts of the individual positively charged fragments against the $[Cu(II)]_0/[Cu(I)]_0$ ratio. Each bar represents the counts for one specific fragment mass. We show 6 counts for the 6 most important fragments per batch. Notably, the number of counts was similar for the four batches. By analyzing the fragment intensities of the six main fragments from the four $[Cu(II)]_0/[Cu(I)]_0$ ratios we used to graft PNIPAM from the surface, we can unambiguously identify all films to be PNIPAM.

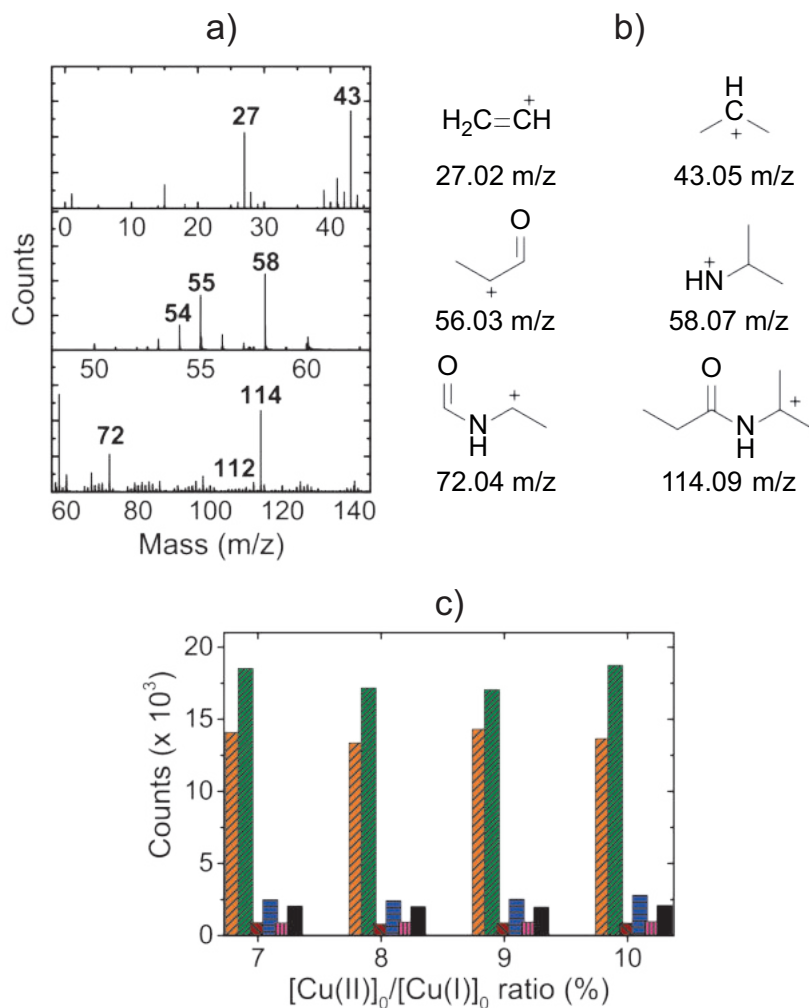


Figure 2.8: (a) Positively charged fragments of the PNIPAM layers on silicon measured by ToF-SIMS. The scale of the y-axis of the three graphs are in counts. Black bars represent the measured fragment masses; (b) Fragments expected from literature (for references see text), the corresponding chemical structures of the fragments are shown above the masses; (c) Counts per fragment as a function of the $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio from ToF-SIMS. The counts for the fragments with increasing m/z are shown from left to right starting with m/z 27 in orange (diagonally hatched), at m/z 43 in green (densely diagonally hatched), at m/z 55 in brown (diagonally hatched), at m/z 58 in blue (horizontally hatched), at m/z 72 in pink (vertically hatched) and for one monomer with the mass of 113 m/z in black.

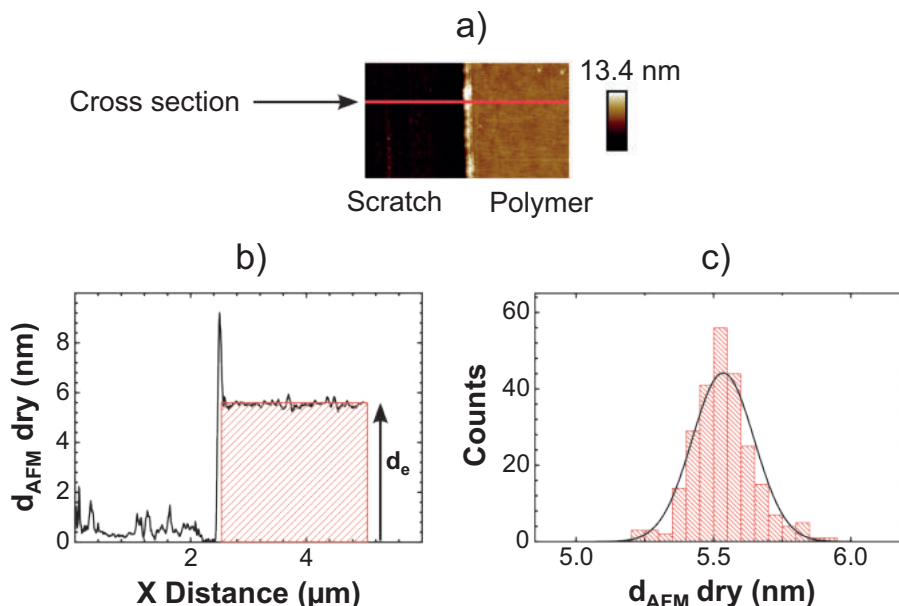


Figure 2.9: (a) AFM tapping mode height image of a dry PNIPAM brush layer on a silicon substrate fabricated at a $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio of 10%. The horizontal scan size is $5\ \mu\text{m}$. The sample was scratched on the left hand side to measure the step height from silicon substrate to the polymer film. The red line indicates the cross section for analyzing the step height, showed in (b); (c) Histogram of the dry polymer thickness variation fitted with the Gaussian (black curve).

2.3.4 Brush characterization with AFM

To demonstrate that our procedure leads to relatively homogeneous sub-ten-nanometer layers, we used AFM tapping mode to study the thickness of the functionalized substrates. The grafted films were scratched by a teflon-coated tweezer to remove the polymer from the substrate and allow for direct thickness and roughness determination by surface imaging. Brush thickness values were measured for dry (this section) and wet (see grafting density section 2.3.5) grafted films. In Figure 2.9(a) an AFM height image of one of the thinnest sample is shown. The left side of the image represents the scratched area (dark color), whereas the right side – the surface of the brush film (bright color). The phase images (not shown) confirmed a successful material removal from the silicon wafer (high contrasted bi-phase). A representative cross sections of the scratched sample is presented in Figure 2.9(b). The lowest point addresses the bare silicon wafer; some profile variation is visible due to the residual polymer content. The highest plateau in the plot corresponds to the brush surface; a characteristic pile-up (peak profile) is also visible as a result of material plowing. By measuring the step height, the polymer brush thickness was determined. Several samples have been analyzed and random positioned cross section have been performed to

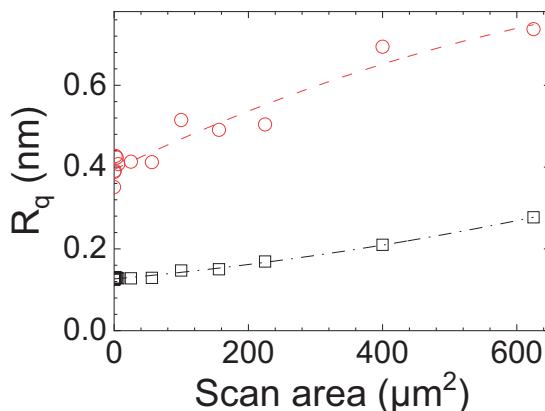


Figure 2.10: Root mean square roughness (R_q) as function of scan area in μm^2 . The bare silicon substrate is compared with the polymer brush layer of PNIPAM. The R_q for the silicon substrate and the polymer layer are plotted in black squares and red dots, respectively.

determine the thickness of the dry film; the distribution is plotted as histogram in Figure 2.9(c). The data were fitted with a Gaussian distribution. The polymer layer thickness d varied between $d = 5.3$ and 6 nm with a mean of $5.5 \text{ nm} \pm 0.3$ nm.

Additionally, we analyzed the root mean square roughness R_q for the polymer brush surface by scanning areas of different sizes (see Figure 2.10). We observe a very small increase of R_q for the polymer brush layer compared to the bare silicon substrate. A slightly increasing trend can be observed by comparing the polymer brush layers with a silicon substrate, while the brush surface shows a “slowing down” of the roughness increase with increasing scan size. We assume that the roughness for a dried polymer film is higher than for a bare silicon substrate due to a statistical variation of monomer attachment to the surface, and due to the random conformation of the grafted polymer molecules. The underlying ATRP initiator has a slight impact on the roughness as well. Additionally, the kinetics of the drying process may also result in lateral heterogeneities that can contribute to surface roughness.

2.3.5 Grafting density

For a structural characterization of a polymer brush the grafting density and the chain length are essential. For a direct chain length analysis, the polymer brush should be cleaved from the silicon substrate, *e.g.*, by using acid hydrolysis [129]. The small amount of material can then be analyzed by GPC or by another direct molar mass analysis method *ex situ*. However, it is rather difficult to determine the grafting density for thin polymer layers grafted from the surfaces by conducting such a direct analysis, due to the fact that the amount of polymer chains is very small. Therefore, we estimate the grafting density of PNIPAM

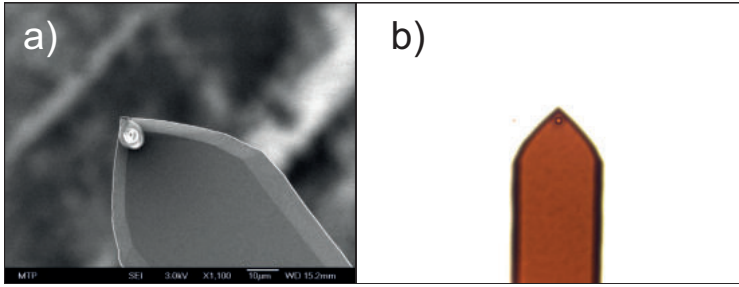


Figure 2.11: (a) Scanning electron (SEM) and (b) optical microscopy images of polystyrene-based colloidal probe cantilever (used for AFM measurements in contact mode).

Table 2.2: Swelling Ratio of PNIPAM Brushes as a Function of their Layer Thickness

Dry thickness h_{dry} nm (tapping mode AFM) ^a	Wet thickness h_{wet} nm (colloidal probe AFM)	Grafting density σ chains/nm ²	Molar mass M g/mol ^b	Radius of gyration R_g (nm)	Reduced grafting density Σ
6.3 ± 0.3	19.5 ± 1.1	0.19	8,200	2.2	3
9.5 ± 0.3	41.7 ± 1.7	0.11	17,600	3.5	4.3

^aCalculated as one standard deviation from AFM image analysis.

^bCalculated by assuming a completely stretched polymer chain.

brushes from the swelling ratio between the dry and the swollen states, respectively [130]. In a previous study the force effect on a PNIPAM layer thickness was shown by performing force–volume measurements recorded in situ at several temperatures in the range 30–36 °C [131]. This required a precise thickness determination of the grafted layers. We note that the thickness obtained by AFM may strongly depend on the operating conditions, *e.g.*, set point and limited contact area (sharp nano-sized AFM tip), due to chain compression effects. Hence, we chose the contact mode imaging with a soft cantilever employed with a micro-sized colloid (see Figure 2.11) to minimize those drawbacks. In Figure 2.12 we plot the wet thickness of a swollen polymer layer against the lateral X distance. The black curves represent eight cross sections along the scan area. We observed, similar to AFM measurements in the dry state, an inhomogeneous scratching of the polymer layer. From the swelling experiments in water we observed a highly stretched behavior of our PNIPAM chains compared to the thickness in dry state. The swollen polymer thickness was averaged for a scan size of 3 μm . The polymer layer thickness becomes significantly higher after adding the solvent (water) to the polymer films. We present two polymer substrates in the wet state and we show the averaged wet thickness measured for 3 different spots per sample in Table 2.2. The grafting density was found to be between 0.11 and 0.19 chains

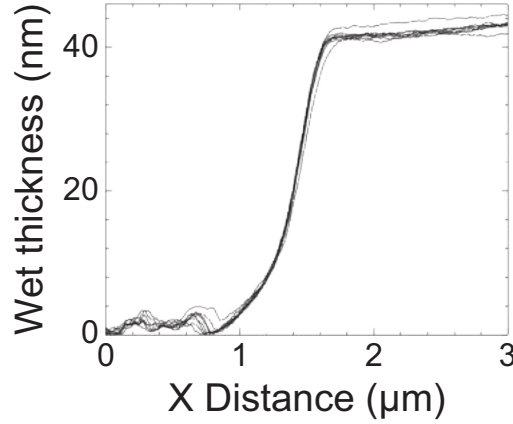


Figure 2.12: Cross section profiles of a wet PNIPAM brush layer on a silicon substrate measured in contact mode AFM in water using a colloidal probe cantilever with 5 μm polystyrene bead. The wet thickness in nm is plotted against the X distance in μm . The sample was scratched to measure the step height from silicon to the swollen polymer film. Curves represent 8 cross sections taken along the scan area.

per nm^2 using the relation [130]

$$h_{\text{wet}}/h_{\text{dry}} = 1.03/\sigma^{(2/3)}, \quad (2.1)$$

where h_{wet} is the wet thickness, h_{dry} the dry thickness and σ the grafting density. Independently of the first estimation of the grafting density, we calculated the grafting density based on the dry thickness via a different route [132, 133]: for a dry layer thickness of 6.3 nm and a molar mass of 8200 g/mol we calculated a grafting density of 0.51 chains/ nm^2 (0.36 chains/ nm^2 for a dry thickness of 9.5 nm respectively) in reasonable agreement with the determination above. This confirms the estimation of the grafting density. The reduced tethered grafting density Σ is defined as

$$\Sigma \equiv \sigma \pi R_g^2, \quad (2.2)$$

where R_g is the radius of gyration, with $R_g = 0.17N^{3/5}$ [63, 64], with N the total number of monomers in a polymer brush chain. The density Σ is used to judge whether the grafted polymer layer indeed fulfills the brush-like character of the grafted polymer film. Since sparse high molar mass chains can also yield thin dry PNIPAM films it is crucial to determine the grafting density. We observed Σ between 3 and 4.3 chains per area that a free non-overlapping polymer chain would occupy under the same temperature and solvent conditions. In general, three regimes exist for polymer grafts, firstly, the “mushroom” or weakly interacting regime ($\Sigma < 1$), secondly the “mushroom-to-brush” regime ($1 < \Sigma < 5$), and thirdly the brush regime ($\Sigma > 5$). The “true brush” regime is defined at significantly high stretching of the polymer chains at typically $\Sigma > 5$. From our results we conclude that our procedures lead to chains in the “mushroom-to-brush” transition regime. Finally we note that for shorter reaction times of our

procedure the thickness at a given $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio would decrease. However, in this case one would further shift the molar mass towards the mushroom regime.

2.4 Summary and outlook

We have demonstrated a reproducible procedure to graft ultra-thin PNIPAM layers from silicon by varying the $[\text{Cu(II)}]_0/[\text{Cu(I)}]_0$ ratio. The results show that our approach leads to grafts in the “mushroom-to-brush” transition regime. The grafted layers we describe here can be employed in surface functionalization in applications where a distance confined by a thickness is explored, such as precisely positioning light emitters at the exterior surface of the brush from the underlying substrate.

CHAPTER 3

Covalent attachment of lead sulfide quantum dots to poly(glycidyl methacrylate) polymer brushes

The covalent attachment of lead sulfide quantum dots to poly(glycidyl methacrylate) (PGMA) polymer brushes is presented. Surface-initiated atom transfer radical polymerization (SI-ATRP) was used to graft PGMA brushes from silicon substrates. Lead sulfide quantum dots with poly(ethylene glycol)-amine functional groups were reacted to the brush layers to establish stable particle attachment. Atomic force microscopy (AFM) and ellipsometry showed that the polymer grafts were homogeneous and the thickness could be controlled between 5 and 33 nm. Additional evidence for successful quantum dot attachment was provided by AFM and fluorescence experiments.

3.1 Introduction

Semiconductor nanoparticles such as quantum dots (QDs), gained much attention as luminescent materials in the past decades. Their use can be found in optical microcavities [134], sensing applications [135, 136], television [137, 138] and many more. QDs have narrow emission spectra that can be tuned by the size of the nanocrystals. Compared to organic dyes, quantum dots have a high photochemical stability which can be crucial for the use as fluorescent labels [27, 139].

By attaching QDs to a surface, it is possible to control the position and the density of nanoparticles. Covalent attachment of QDs to a polymer layer for instance reduces particle aggregation, weakly attached particles can be removed after washing steps, and the particles will less likely infiltrate the polymer brush layer [140]. The position of an emitter with respect to a surface will strongly influence the emission properties [14].

Since our aim is to precisely position QDs inside 3D silicon photonic crystals, a thoughtful strategy is needed. Many studies can be found in the literature that tackle the covalent attachment of quantum dots to a polymer layer [141–144]. These coupling strategies are based on an activation step either on the polymer layer or on the quantum dot before actual covalent attachment of the particles takes place. Since it is challenging to ensure a successful activation step of the polymer layer covering the pores of a photonic crystal and to clean

the pores in the silicon from impurities, we aimed for a coupling strategy which circumvents additional reaction steps. Additionally silicon is almost transparent for the emission wavelength range of PbS quantum dots such that the emission can be detected with a minor loss. We employ near-infrared emitting lead sulfide (PbS) quantum dots, because their optical properties match the band gap of the photonic crystals we plan to use. These are coupled covalently to a poly(glycidyl methacrylate) layer. PGMA was chosen for its epoxide side chains which can be used as functional groups to couple amine-PEGylated lead sulfide quantum dots.

Here, we show the covalent attachment of amine-functionalized lead sulfide quantum dots to a polymer brush layer made of poly(glycidyl methacrylate). By making use of the epoxide-amine coupling mechanism the quantum dots can be attached to the silicon substrates to control particle density and particle homogeneity. The particle density on the polymer film was studied as a function of reaction and rinsing conditions with the aim to reach the highest possible stability. The thickness and the homogeneity of the polymer brush were studied with AFM and ellipsometry. The particle density was studied with AFM.

3.2 Materials and methods

3.2.1 Materials

Sulfuric acid (H_2SO_4 , 95-97%) for the piranha solution was received from Sigma-Aldrich. Hydrogen peroxide was used as an aqueous solution (H_2O_2 , 30 wt% in water, Merck). Glycidyl methacrylate (GMA, 97%, Sigma-Aldrich) was filtered over basic aluminum oxide to remove the inhibitor monomethyl ether hydroquinone. Copper(I) chloride (CuCl , Sigma-Aldrich, 97%) was purified by stirring in glacial acetic acid (Sigma-Aldrich, $\geq 99.5\%$), filtering, and washing with ethanol (Biosolve, 96%) three times. The catalyst was dried under vacuum at room temperature for 48 h. Copper(II) bromide (CuBr_2 , Sigma-Aldrich, $\geq 99\%$), methanol (Biosolve, 99.8%), 2,2-bipyridyl (BiPy, Sigma-Aldrich, 99%), 2-bromo-2-methylpropionic acid allyl ester (Sigma-Aldrich, 98%), hexachloroplatinic acid (Sigma-Aldrich, 99.9%), dimethylchlorosilane (Sigma-Aldrich, 98%) and anhydrous dimethyl sulfoxide (Sigma-Aldrich, 99.9%) were used as received. Millipore Milli-Q grade (resistivity $> 18 \text{ M}\Omega\text{cm}$) water was used in the experiments. The PEG-amine functionalized lead sulfide (PbS-PEG-NH_2) and cadmium selenide/zinc sulfide (CdSe/ZnS-PEG-NH_2) quantum dots were used as received from Suzhou Xingshuo Nanotech Co., Ltd. in dry state. 10 mM phosphate-buffered saline (PBS) at $\text{pH} = 7.2$ was prepared for the dilution series of the quantum dot stock suspensions. The PBS was made from 8 g NaCl (137 mM), 0.2 g KCl (2.7 mM), 1.44 g Na_2HPO_4 (10 mM), and 0.24 g KH_2PO_4 (2 mM) in 800 mL water and the pH was adjusted with HCl.

3.2.2 Sample fabrication

The sample fabrication process can be divided in three parts. Firstly, the preparation of silicon wafers and the attachment of the initiator to these silicon wafers

is presented. Secondly, the SI-ATRP of the poly(glycidyl methacrylate) brushes is shown. And thirdly, the attachment of near-infrared emitting lead sulfide quantum dots to the grafted poly(glycidyl methacrylate) brushes is discussed.

Chemical vapor deposition of the initiator

The initiator was prepared following the procedure explained in Chapter 2. A silicon wafer was cut into nine $1.2\text{ cm} \times 1.2\text{ cm}$ wafer pieces. A piranha solution was prepared with the ratio of 3 parts H_2SO_4 to 1 part H_2O_2 (volume ratio, v/v%). The nine silicon wafer pieces were placed into the sample holder. The sample holder was lowered gently into the piranha solution and the samples were cleaned for 30 min. The wafer pieces were rinsed 10 times with water and ethanol. The desiccator was attached to a vacuum pump for 5 to 10 min. The initiator was taken from the vial using an argon-purged syringe. A few droplets of initiator (30 μL) were placed inside a small plastic petri dish that was placed in the middle of a desiccator. The wafer pieces were placed around the petri dish. The desiccator was attached to a vacuum pump for 15 min. After 15 min the valve was closed and the desiccator was removed from the pump. The chemical vapor deposition (CVD) process was allowed to proceed for 16 h. Thereafter, the samples were placed in a flask with 100 mL toluene in an ultrasonication bath for 20 s to remove excess of initiator. Each substrate was rinsed 10 times with ethanol and water before the substrates were dried under a nitrogen stream. The samples were stored in a nitrogen box.

Chemical synthesis of PGMA polymer brushes

GMA (10 mL, 75 mmol) monomer and BiPy (282 mg, 1.81 mmol) were added to a mixture of water (2 mL) and methanol (8 mL) [145]. The solution was purged with argon for 30 min under continuous stirring. CuCl (72.8 mg, 0.74 mmol) and CuBr_2 (7.8 mg, 0.035 mmol) were added to another flask and flushed with argon for 15 min. The monomer solution was transferred by a previously flushed syringe to the catalyst flask. The resulting polymerization solution was stirred for an additional 30 min under argon. Afterwards the solution was transferred to the reaction flasks containing the substrates. The polymerization was allowed to proceed for 60 min. The substrates were cleaned extensively with acetone and water-free dimethyl sulfoxide to remove non-reacted monomer, metal complex, and remaining catalyst residues. The substrates were dried in a nitrogen stream to obtain the samples with the thin PGMA brush film.

Quantum dot coupling

For the coupling of amino-PEGylated lead sulfide quantum dots to the PGMA brushes, a quantum dot suspension was prepared by adding a desired amount of quantum dot stock solution together with 5 mL of PBS buffer $\text{pH} = 7.2$ at $50\text{ }^\circ\text{C}$. The suspension was filtered twice and purged with nitrogen for 15 min. The substrates were placed in a vial and the concentration of quantum dot suspension was varied for a total volume of 2 mL to study the particle density depending on the used concentrations. The reaction was allowed to proceed for 4 h at $50\text{ }^\circ\text{C}$.

Table 3.1: Concentrations used for each sample.

Sample name (batch - time - sample number)	Concentration
PbS-PEG-NH ₂	
2-15-1	10 nM
2-15-2	0.33 nM
2-15-3	0.1 nM
PbS-PEG-NH ₂	
3-60-1	10 nM
3-60-2	3.33 nM
3-60-3	1 nM
PbS-PEG-NH ₂	
4-60-1	20 nM
4-60-2	15 nM
4-60-3	10 nM
CdSe/ZnS-PEG-NH ₂ (green emitting)	
3-30-1	20 nM
3-30-2	6.66 nM
3-30-3	2 nM
CdSe/ZnS-PEG-NH ₂ (red emitting)	
4-15-1	20 nM
4-15-2	6.66 nM
4-15-3	2 nM

The concentrations of the suspensions used for each sample are shown in Table 3.1.

3.2.3 Characterization

Atomic force microscopy

AFM measurements were performed in tapping mode in order to determine the dry brush thickness and the roughness using the Multimode 8 AFM retrofitted with the NanoScope V controller and the JV vertical engage scanner (Bruker, Santa Barbara, CA, USA). In tapping mode, commercially available, silicon cantilevers (model NCH, NanoWorld, Switzerland) with a high frequency (320 kHz), with a nominal spring constant of 42 N/m and a nominal tip radius of 8 nm (shape of polygon based pyramid) were used. The scanning was performed at a scan rate of 0.5 Hz with the ratio of set point amplitude to free oscillation amplitude of about 0.75. To perform step height measurements, the surface of the polymer brush substrate was scratched with a teflon-coated tweezer. The scratching was performed at regular spacing between lines in order to create a grid. This way it was easier to find a scratched area to measure the step height. Using analysis software cross sections were taken and the height between the scratch and the polymer brush area was measured. For each image 512 measurements per line

for each scan size are taken. The scan sizes were 50 μL , 25 μL , 10 μL , 5 μL , 2.5 μL , 1 μL , and 500 nm.

Contact angle measurements

Static contact angles of a 4 μL water sessile drop were measured on flat 2D silicon substrates (OCA15, Dataphysics, Germany). The contact angles were manually fitted.

Ellipsometry

The dry thickness of a surface-grafted PGMA film was determined by a variable-angle spectroscopic ellipsometer (VASE ellipsometer base model, LOT Oriel GmbH, Darmstadt, Germany) at three different angles of incidence (65° , 70° , and 75°) at room temperature. Five locations were measured for each sample to determine an average polymer layer thickness. The thickness was determined *via* the analysis of a three-layer (Si/SiO₂/PGMA) model with known thicknesses of the Si and SiO₂ layers and known refractive indices of the Si and SiO₂ layers (software WVASE32, LOT Oriel GmbH, Darmstadt, Germany).

Fluorescence microscopy

The in the visible wavelength range emitting CdSe/ZnS quantum dots were analyzed by fluorescence microscopy using an inverted research microscope (Olympus IX71, Melville NY, USA) equipped with a X-Cite Series 120 EXFO (120 W lamp, in combination with Olympus TH4-200) as light source and a digital camera with 12.5 million pixel (Olympus DP71). The software used for the imaging was Cell[^]D (ver. 3.1, Build 1276). Imaging of the 532 nm emitting CdSe/ZnS quantum dots was performed with excitation light of $\lambda = 460$ nm and the fluorescence was measured at $\lambda = 535$ nm. Imaging of the 627 nm emitting CdSe/ZnS quantum dots was performed with excitation light of $\lambda = 540$ nm and the fluorescence was measured at $\lambda = 630$ nm. All measurements were done using an integration time of 20 s by using a 10-fold magnification objective.

Fourier-transform infrared spectroscopy

A Vertex 70v FT-IR instrument (Bruker) was used to measure the polymer brush layer on the silicon substrates [146]. Figure 3.1 shows the spectra for two different types of lead sulfide quantum dots that had a different organic shell. For each measurement a droplet of suspension was measured without letting the solvent evaporate.

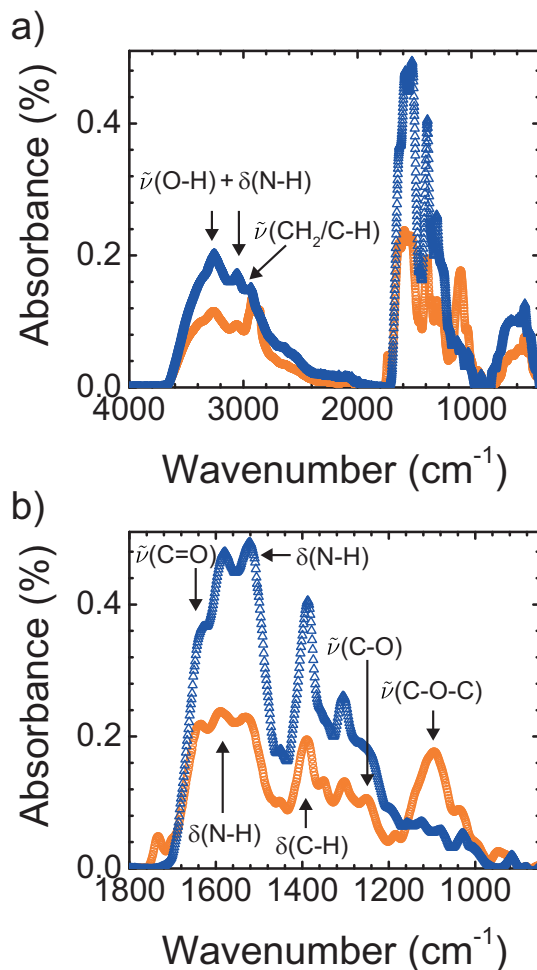


Figure 3.1: FT-IR spectrum of lead sulfide quantum dots: a) Spectra of PEGylated amine-functionalized PbS (orange) and glutathione-functionalized PbS (blue) from 4000 till 400 cm^{-1} . b) Spectra between 1800 and 850 cm^{-1} .

Figure 3.1(a) shows the full spectra for both types of lead sulfide quantum dots. The blue data represents the glutathione functionalized PbS quantum dots and the orange data the PbS-PEG-NH₂ material. The stretching vibrations for the OH-bonds, the deformation vibrations for the NH-bonds, and the stretching vibrations for CH and CH₂ were visible for the glutathione species. For the PbS-PEG-NH₂ quantum dots the deformation vibration for the NH-bonds and the stretching vibrations for the CH and CH₂ were visible. Figure 3.1(b) shows a zoom-in into for range in wavenumber of 1900-850 cm^{-1} . For the glutathione-functionalized PbS quantum dots stretching vibrations for the carboxyl group and the deformation vibrations for NH-bonds and CH-bonds were observed. For the PbS-PEG-NH₂ species the deformation vibrations for NH-bonds and CH-bonds

were observed. The characteristic aliphatic ether bond (C-O-C) and the alcoholic bond (C-O-H) of the PEG unit can be correlated to C-O, C-O-C stretches and C-O-H bends vibrations at about 1251 and 1095 cm^{-1} [147, 148].

FT-IR proved that the specific organic shells were present on the quantum dots such that any further interpretation about a covalent attachment of the quantum dots to the polymer layer was valid. Unfortunately, the sensitivity of the instrument was not sufficient enough to proof the presence of quantum dots on the polymer layer with FT-IR.

3.3 Results and discussion

3.3.1 Polymer layer

PGMA polymer brushes were grafted from silicon substrates *via* surface-initiated atom-transfer radical polymerization to obtain a functional surface. To these grafts lead sulfide quantum dots were attached *via* an epoxide-amine coupling. Figure 3.2 shows the complete process of the sample fabrication. The particle density on the polymer brush layers was varied with the concentration of the quantum dot suspension. In this section we first discuss the characterization of PGMA layers *via* AFM, contact angle measurements and ellipsometry. Since the aim of this study is to attach lead sulfide quantum dots to the polymer layer, we present the evidences for the presence of quantum dots for different conditions of the coupling procedure. We show which conditions are the most suited ones for a successful fabrication of 3D silicon photonic crystals equipped with quantum dots.

After the synthesis, the polymer layers were at first analyzed with ellipsometry. Ellipsometry was used to determine the thickness and the homogeneity of the polymer brush layers. Figure 3.3 shows the polymer brush layer thickness plotted against the polymerization time. The procedure led to a thickness range between 5 ± 2 nm and 33 ± 12 nm, for polymerization times ranging from 10-60 min. Multiple polymerization runs were analyzed. For our final goal of assembling quantum dots inside 3D photonic crystals, it is crucial that the thickness is not too large because the polymer layer would fill and block the pores of the 3D silicon photonic crystals (see Chapters 5 and 6). The thickness control shown here is fully adequate to achieve this.

Contact angle measurements were performed on two polymerization batches in order to characterize changes on the surface of the silicon substrates after each fabrication step. Table 3.2 the static contact angle values obtained after every fabrication step. Before the silicon substrates were cleaned with piranha solution a contact angle of $27^\circ \pm 0^\circ$ was found. After the piranha cleaning step a contact angle of $10^\circ \pm 0^\circ$ was found. The fabrication step of CVD led to a contact angle of $87^\circ \pm 1^\circ$ which is caused by the hydrophobic nature of the ATRP initiator. Once a thin polymer layer of PGMA was grafted from the monolayer the contact angle decreased to $59^\circ \pm 1^\circ$ for a polymerization time of 15 min. For a polymerization time of 60 min the contact angle decreased slightly further to $56^\circ \pm 0^\circ$. After the covalent attachment of PEGylated-amine functionalized lead

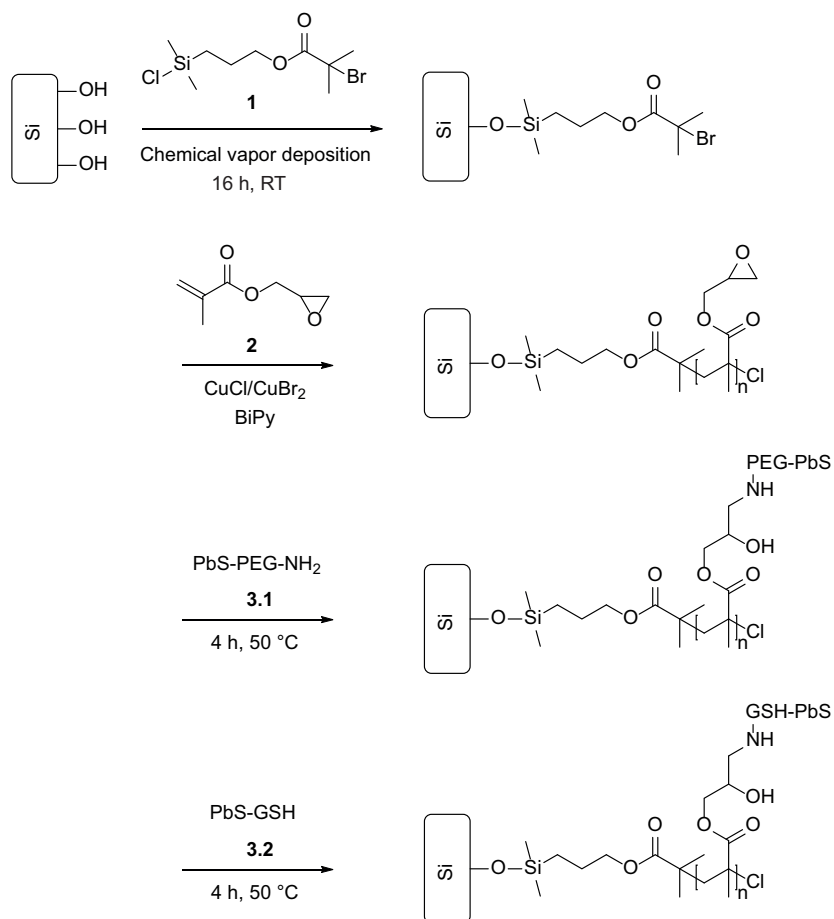


Figure 3.2: General reaction schemes to anchor the ATRP initiator **1** to silicon substrate and to perform ATRP of GMA **2**. Lead sulfide quantum dots are attached to the PGMA brushes by using two different quantum dot ligands, namely a poly(ethylene glycol)-amine ligand **3.1** and a glutathione ligand **3.2**.

Table 3.2: Results of the contact angle measurements. The average angle for each experiment is shown as is the standard deviation.

Fabrication step	Contact angle
Before piranha	27° ± 1°
After piranha	10° ± 0°
After CVD of initiator	87° ± 1°
After 15 min polymerization	59° ± 1°
After 30 min polymerization	59° ± 2°
After 60 min polymerization	56° ± 0°
After coupling PbS-PEG-GSH	50° ± 1°
After coupling PbS-PEG-NH ₂	66° ± 0°

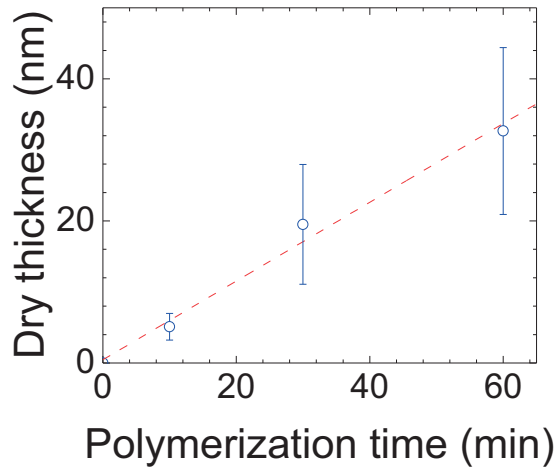


Figure 3.3: Dry thickness of the polymer brush layers plotted against polymerization time measured with ellipsometry. The data points show the averaged thicknesses for a given polymerization time. The red dashed line is the fit through these data points.

Table 3.3: Average step height thickness determined by AFM of the measured samples.

Polymerization time	Step height thickness (nm)	Standard deviation (nm)
30	12.4	2.9
60	29.0	0.8

sulfide quantum dots the contact angle was found to be $66^\circ \pm 0^\circ$. For the other type of PbS quantum dots with a glutathione shell the contact angle was $50^\circ \pm 1^\circ$.

Atomic force microscopy was used to perform step height measurements of the polymer brush layer on two samples made using polymerization times of 30 and 60 min. To perform step height measurements, the surface of the polymer brush substrate was scratched with a teflon-coated tweezer. During the scratching the polymer brush layer was removed and pushed aside forming a sort of wall, while revealing the silicon surface. At different places alongside the edges the surface was scanned using AFM in tapping mode. The average value of the thickness is shown in Table 3.3 for each sample that was measured using AFM. Since the height difference between AFM and ellipsometry is very small, see Chapter 2, subsequent thickness measurements were performed with ellipsometry only because of the shorter measurement time using ellipsometry.

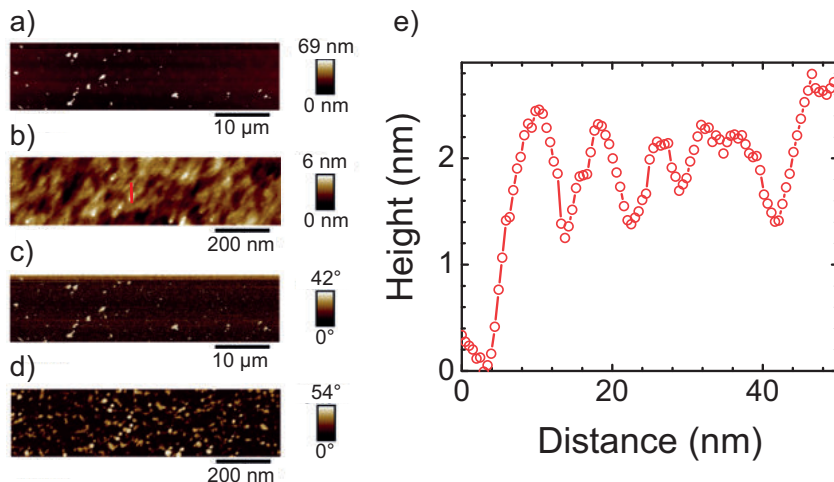


Figure 3.4: AFM images of sample 3-60-2: a) Height image with a scan sizes of 50 μm , b) height image with a scan sizes of 1 μm , c) phase image with a scan sizes of 50 μm , d) phase image with a scan sizes of 1 μm , e) cross section taken from panel b).

3.3.2 Covalent attachment of lead sulfide quantum dots

Three different types of particles were used for the attachment procedure, see Figure 3.2. The first type of particles were PEGylated lead sulfide quantum dots with an amine moiety. PEGylated lead sulfide quantum dots with a glutathione moiety were the second type. The third type of particles were PEGylated cadmium selenide/zinc sulfide quantum dots with an amine moiety. CdSe/ZnS quantum dots were only characterized with fluorescence microscopy as a proof of principle for the coupling procedure. Both types of quantum dots were covalently attached *via* a ring opening of the epoxide on the polymer side chains by the amine moieties as nucleophiles.

After the coupling of quantum dots to the polymer brushes, AFM was used to characterize the surface of the substrates. AFM was used to record height and phase images of the reacted surface. From the height the size of the attached nanoparticles was estimated. With the phase the energy dissipation of the vibrating cantilever was measured. The phase was analyzed to determine if a specific area presents polymer or particle. With both the height and the phase it was possible to conclude if a quantum dot was present on the analyzed area.

Figure 3.4 shows a sample with a polymer thickness of 18.5 ± 3.3 nm that was treated with a quantum dot suspension with a concentration of 3.33 nM of amine-PEGylated lead sulfide quantum dots. The reaction was allowed to proceed for 4 h at 50 °C. On the left side of the image four AFM images are shown (3.4(a-d)). First the height image for a scan size of 50 μm is shown. White spots were visible with a height up to 69 nm. The corresponding phase is shown in panel c). The spots that were visible in panel a) correlate with the phase image in panel c). The observed white spots were most likely aggregates of quantum dots

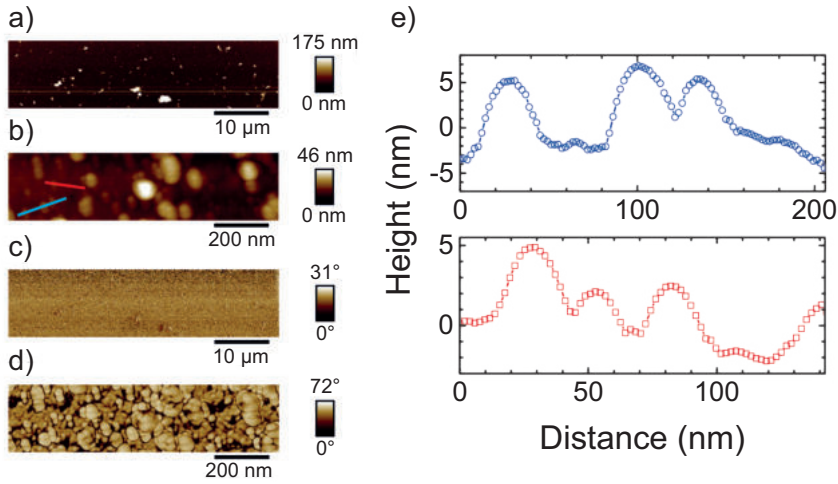


Figure 3.5: AFM images of sample 4-60-1: a) Height image with a scan sizes of 50 μm , b) height image with a scan sizes of 1 μm , c) phase image with a scan sizes of 50 μm , d) phase image with a scan sizes of 1 μm , e) cross sections taken from panel b).

on the surface or contaminations from the fabrication. For a scan size of 50 μm no further details on the coverage of the polymer layer with quantum dots can be discussed. In panel b) a height image is presented for a scan size of 1 μm . The smaller scan area displayed smaller and higher areas randomly distributed on the surface. The phase in panel d) correlated with the height. The red cross section shown in panel b) for the smaller scan size is presented in e). The height of the harder areas was about 2.5 nm larger than for the surrounding surface. Since a typical PbS quantum dot diameter is about 5 nm for the inorganic core it was concluded that there are quantum dots present on the softer polymer brush layer and that the quantum dots were penetrated into the polymer brush. This observation is attributed to a lower polymer brush density making it more likely that the quantum dots were sitting in the polymer brush layer.

Figure 3.5 shows a sample with a polymer thickness of 13.6 ± 0.9 nm that was treated with a quantum dot suspension with a concentration of 20 nM of amine-PEGylated lead sulfide quantum dots. The reaction was allowed to proceed for 4 h at 50 $^{\circ}\text{C}$. Figure 3.5(a) shows a height image with a scan size of 50 μm . White spots were visible in the height image. Similar to the sample shown in Figure 3.4 the observed white spots were aggregations or contaminations. The phase image in panel c) for the same area as in a) was not showing a direct correlation for all of the observed spots. A few spots could be contaminations which would not be visible in the phase image. Figure 3.5(b) shows a height image for a scan size of 1 μm . A few larger spots were visible with a larger height and also smaller spots were observed. Two cross section (blue and red) were analyzed and are presented in Figure 3.5(e). Figure 3.5(d) shows the corresponding phase image. The smaller spots are harder areas compared to the polymer brush layer. Figure 3.5(e) shows the two cross sections of panel b). Spots with a height of

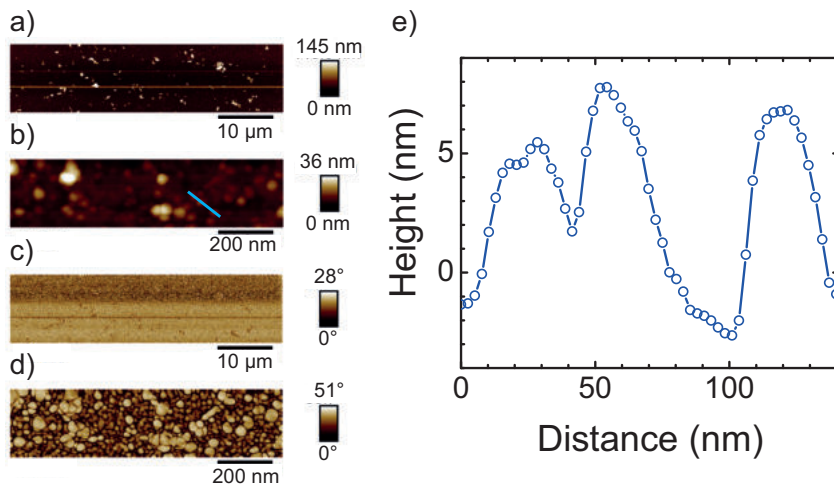


Figure 3.6: AFM images of sample 4-60-2: a) Height image with a scan sizes of 50 μm , b) height image with a scan sizes of 1 μm , c) phase image with a scan sizes of 50 μm , d) phase image with a scan sizes of 1 μm , e) cross section taken from panel b).

about 5 nm were present on the surface for the blue cross section. The values for the height of the spots taken from the red cross section were slightly lower. It can be concluded that the particles might be penetrated into the polymer layer. Compared to a suspension concentration of 3.33 nM we observed from the AFM images for a concentration of 20 nM a higher coverage of quantum dots. Our results were in good agreement with the data from Gupta *et al.*[143] and Tagit *et al.*[144] but showed room for improvement regarding coverage and homogeneity of the particles on the polymer film.

The goal of the experiments using the next sample was to reduce amount and size of aggregates of the quantum dots and to move more into the direction of having individual quantum dots attached to the surface. Figure 3.6 shows a sample with a polymer thickness of 12.7 ± 1 nm that was treated with a quantum dot suspension with a concentration of 15 nM of amine-PEGylated lead sulfide quantum dots. The reaction was allowed to proceed for 4 h at 50 °C. Figure 3.6(a) shows a height image for a scan size of 50 μm . The large scan area displayed aggregations or contaminations on the surface. Figure 3.6(b) shows a smaller scan size of 1 μm . Smaller spots were visible and the phase image in Figure 3.6(d) correlated well with the height. In the phase image in Figure 3.6(d) many small spots were visible on the surface. The cross section from panel b) is presented in Figure 3.6(e). The height of the spots was about 5 nm. These values match with the estimated quantum dot size of 5 nm. Compared to a suspension concentration of 20 nM, that was previously shown in Figure 3.5, a used concentration of 15 nM led to a more homogeneous coverage of quantum dots close to a densely packed monolayer. Sample 4-60-2 showed the highest coverage of nanoparticles on the surface by limiting aggregation at the same time.

From the AFM images we observe features of approximately 2-8 nm in height.

These are attributed to quantum dots. Multilayers were not observed (only a few aggregates), and only a (sub)monolayer of particles, and therefore we conclude that the particles only stay when connected to the polymer layer, but not physisorbed on top of already bound particles. The larger scan sizes mostly showed a few aggregates and from a smaller scan size it was sometimes possible to derive the shape of individual quantum dots. Due to the shape of the cantilever the measured lateral size is useless for further analysis or interpretations. The phase image, however, gave the same information regardless of the different scan sizes.

A concentration of 15 nM of PEGylated lead sulfide quantum dots (with an amine moiety) at 50 °C proved to be the best condition to end up with a homogeneously and densely covered polymer sample. Figure 3.6(b) shows the height and Figure 3.6(d) shows the phase for a scan size of 50 μm . The amount of aggregates is very low. The second best condition is a concentration of 20 nM of PEGylated quantum dots. Figure 3.5(b) and Figure 3.5(d) present for the same scan size a less homogeneously covered polymer layer. The amount of aggregates is a lot higher. All other samples with PEGylated lead sulfide quantum dots or with a glutathione moiety were not successful enough regarding coverage and homogeneity and thus these are not further discussed here. A concentration of 15 nM of quantum dots at 50 °C was used for the fabrication of the samples used in Chapter 6 and Chapter 7.

3.3.3 Fluorescence microscopy with quantum dots

In order to get a proof of principle for optical visibility of the QDs after the coupling reaction, the coupling was performed with quantum dots that emit within the visible wavelength range. Figure 3.7 shows fluorescence microscopy images for CdSe/ZnS quantum dots attached to a PGMA layer by using the optimized conditions as discussed above for PbS quantum dots. Two types of CdSe/ZnS quantum dots were used. The first type of quantum dots had an emission wavelength of 532 nm (green) the second one an emission wavelength of 627 nm (red). Figure 3.7(a) shows the fluorescence microscopy image for the green-emitting quantum dots. The polymer layer was functionalized with the quantum dots by using the procedure with a quantum dot concentration of 15 nM. Aggregates and slight contaminations were visible on the sample. Figure 3.7(b) shows the autofluorescence of a reference sample with a polymer layer thickness of 6.8 ± 2.2 nm at $\lambda = 535$ nm. It can be seen as the background measurement of the setup. The intensity is similar to the sample with attached quantum dots. There can be several reasons for the absence of an increase of the intensity. It is possible that the change in intensity can not be detected accurately enough. Secondly, the density of attached quantum dots was very low or the covalent attachment was not successful. Since the quantum dots sit on a thin polymer layer close to the interface, where the emitter and the interface have different refractive indices, the local density of states is modified due to interference of the emitted and reflected light [149, 150]. Quenching by the interface can occur for quantum dots *via* nonradiative energy transfer [144, 151]. Figure 3.7(c) shows a sample with red-emitting CdSe/ZnS quantum dots. The coverage in the center

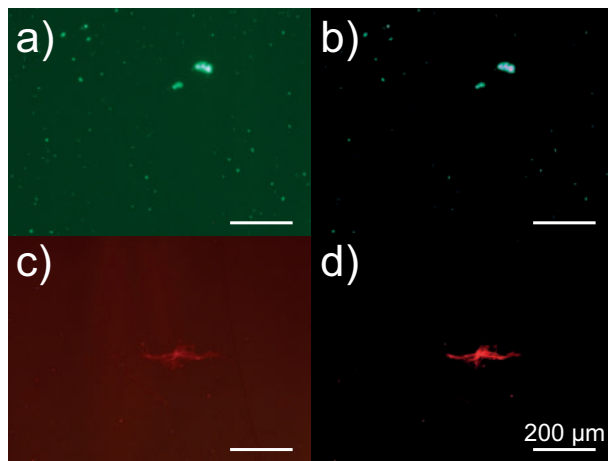


Figure 3.7: Fluorescence microscopy on CdSe/ZnS quantum dots: a) Green-emitting CdSe/ZnS quantum dots attached to a sample with a polymer layer thickness of 3.1 ± 0.1 nm at $\lambda = 535$ nm, b) native / autofluorescence of a reference sample with a polymer layer thickness of 6.8 ± 2.2 nm at $\lambda = 535$ nm was subtracted from a), c) red-emitting CdSe/ZnS quantum dots attached to a sample with a polymer layer thickness of 4.8 ± 0.4 nm at $\lambda = 630$ nm, d) native / autofluorescence of a reference sample with a polymer layer thickness of 6.8 ± 2.2 nm at $\lambda = 630$ nm was subtracted from c). The contrast of the image was increased for better visibility.

of the image was slightly inhomogeneous compared to the rest of the sample. Figure 3.7(d) shows the autofluorescence of a reference sample with a polymer layer thickness of 6.8 ± 2.2 nm at $\lambda = 630$ nm. As seen for the green-emitting quantum dots, the intensity only changes slightly before and after the attachment of the quantum dots to the polymer layer.

With two different types of CdSe/ZnS quantum dots, that had the same PEGylated-amine functionalized inorganic core as the lead sulfide quantum dots, a proof of principle was achieved. Besides the AFM studies the fluorescent microscopy results confirmed a successful procedure to covalently attach quantum dots to a PGMA layer.

3.4 Summary and outlook

We have described a procedure to attach lead sulfide quantum dots to thickness-controlled PGMA layers. We have shown that the density of quantum dots attached to the polymer layer can be controlled by temperature and the concentration of the used quantum dot suspension. The large advantage of the used procedure is the straight forward coupling mechanism to make use of the reactive epoxide groups present within the PGMA polymer chains. This way no further activation step is required to covalently attach the nanoparticles to the brush. Proof of principle optical measurements were performed using CdSe/ZnS QDs

emitting in the visible wavelength range, which provided an indication that the coupling strategy was a success. To increase the intensity of the emitted light from CdSe/ZnS attached to a polymer layer for fluorescence microscopy imaging, the polymer layer thickness could be increased to modify the local density of states and to prevent quenching by the interface. For the lead sulfide quantum dots optical measurements were performed by a different setup. The results of these experiments can be found in Chapter 7.

CHAPTER 4

Broadband emission rates of near-infrared PbS quantum dot nanocrystals

In pursuit of functionalizing 3D silicon nanophotonics with optically active building blocks, we investigate as candidates near-infrared (NIR) emitting semiconductor quantum dot (QDot) nanocrystals. We present continuous-wave and time-resolved spectral emission of different commercially obtained lead sulfide quantum dots with two different cappings - polyethylene glycol (PEG) and oleic acid (OA) - that are suspended in either water, chloroform, or toluene. The emission spectra reveal maxima at different photon energies, as set by the nanocrystals' average diameters. Time-resolved emission histograms reveal varying amounts of non-exponential decay, all of which are successfully modeled with a log-normal distribution of decay rates. We observe for quantum dots with OA surface groups that the most frequent decay rate varies slightly with photon energy and concomitant quantum dot diameter. The rates agree with a two-level exciton model, especially if we assume the transition dipole moment to vary proportionally to the quantum dot diameter, but not with an atomic-like dipole emitter. For quantum dots with PEG surface groups, the most frequent decay rate decreases remarkably beyond photon energies of 8000 cm^{-1} or conversely for nanocrystal diameters below 4.4 nm. As possible hypotheses for these remarkable observations, we discuss quenching in general, solvent polarity, solvent resonance (vibrational and electronic), acoustic modes, electron or hole wave function trapping, all of which can be excluded. As a first step towards silicon nanophotonics, we study quantum dots dip-coated on a silicon surface, and observe that the emission rates are markedly increased by 5- to 10-fold, which is attributed to the higher dielectric function near to the silicon surface compared to suspensions.

4.1 Introduction

Quantum dots are semiconductor crystals of nanometer dimensions with characteristic optical properties that are determined by their size. Since their diameters are comparable or even smaller than the extent of the electron and hole wave func-

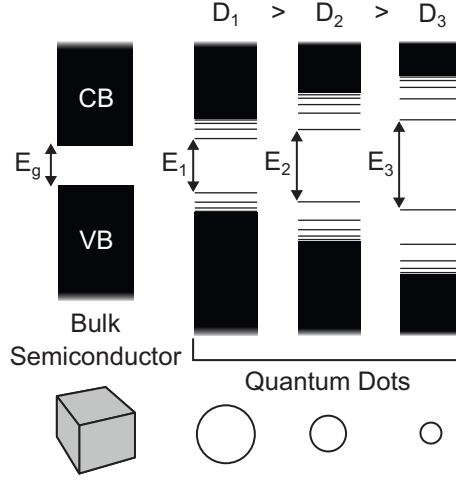


Figure 4.1: Left: in a bulk semiconductor, the valence band (VB) and conduction band (CB) are separated by the band gap energy E_g . With decreasing quantum dot diameter ($D_1 > D_2 > D_3$), the ground-state exciton energy increases: $E_1 < E_2 < E_3$. Both hole levels near the VB and electron levels near the CB are discrete. Figure adapted from Ref. [152].

tions, the wave functions are quantum confined, revealing characteristic discrete energy levels, as opposed to the continuum levels in bulk semiconductors [23–26, 153, 154], as illustrated in Figure 4.1. The properties of electrons (at high energies in the conduction bands) and holes (at low energies in the valence bands) are effectively described by the well-known quantum-mechanical particle-in-a-box model. Due to quantum size confinement, the electron levels are shifted up with decreasing quantum dot diameter and the hole levels shifted down, leading to an increase (or blue shift) of the exciton energy, see Figure 4.1. These properties have allowed to synthesize light emitters with a desired range of photon energies, which has contributed to the great popularity and proliferation of quantum dot nanocrystals [24–26, 153], culminating in the 2023 Nobel prize to Bawendi, Brus and Ekimov.

The choice of a certain sample of quantum dots for one’s favorite application is crucial since the emission spectrum depends not only on the size but also on the material. In our case, the research goal is to pursue active silicon nanophotonics using quantum emitters [35, 155]. Therefore, we develop 3D silicon photonic band gap crystals and place quantum dot emitters deep inside the nanostructure to explore advanced quantum optics of a 3D photonic band gap [156–159]. Since silicon nanostructures have a transparency range limited to 1.1 eV due to the electronic band gap, quantum dots preferably emit below 1.1 eV to avoid absorption, hence our choice towards PbS or PbSe quantum dots [160]. We decided to perform our studies with PbS quantum dots as they are commercially available with a variety of organic ligands that allow to attach quantum dots at targeted

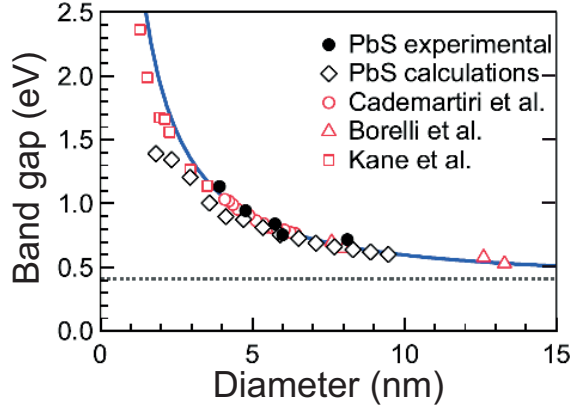


Figure 4.2: Relation between the PbS quantum dot band gap and the nanocrystal diameter, adapted with permission from Moreels *et al.* (Size-dependent optical properties of colloidal PbS quantum dots, ACS Nano, 2009, 3 (10), 3023-3030. Copyright (2018) American Chemical Society.) Black circles are measurements from Moreels *et al.*, red circles from Cadematiri *et al.* [162], red triangles from Borrelli and Smith [163]. Black diamonds are calculations of Moreels *et al.*, and red squares from Kane *et al.* [164]. The drawn curve is a sizing curve matched to all experimental and theoretical data, and the horizontal dotted line the bulk PbS band gap $E_g = 0.41$ eV.

positions inside a nanophotonic structure [161]. Furthermore, the organic ligand can have positive effect on the quantum efficiency of the nanocrystal and can stabilize or protect the inorganic core.

Figure 4.2 shows that the band gap of PbS quantum dot nanocrystals decreases with increasing diameter, as expected. Moreels *et al.* compiled several data sets of experimental and theoretical data [165], where the band gap is determined from optical absorbance spectra and the diameter from electron microscopy. The experimental data from Moreels *et al.* agree well with those of Cadematiri *et al.* [162] and with those of Borrelli and Smith [163], even though the latter are different nanocrystals embedded in glass. Since the diameter of the nanocrystals is less than twice the PbS exciton Bohr radius ($R_{\text{Bohr}} = 18$ nm), the exciton wave functions are quantum confined [166, 167], leading to PbS nanocrystal band gaps exceeding the $E_g = 0.41$ eV bulk PbS band gap, in agreement with expectation, see Figure 4.1. The experimental observations also agree well with tight-binding calculations of both Moreels *et al.* and Kane *et al.* [164]. From all data combined, Moreels *et al.* derived a sizing curve that yields the nanocrystal diameter from the optically measured band gap.

Commercially, PbS quantum dots were found to be available with emission in the range 0.8 to 1.4 eV corresponding to wavenumbers $6450 < \tilde{\nu} < 11500$ cm^{-1} , or wavelengths $880 < \lambda < 1550$ nm. Since we study samples of PbS quantum dots from different suppliers, we want to characterize the emission range of the dots to match with the 3D photonic band gap. In the interest of time-resolved quantum optics experiments, we also characterize the emission dynamics. From

the combined data we aim to infer general behavior of PbS nanocrystal quantum dots.

4.2 Materials and methods

4.2.1 Optical setup

The setup that was used to collect the emission spectra and frequency-resolved and time-resolved emission measurements is described in detail in Ref. [155] and in Chapter 7. The sample holder was adapted since the quantum dot suspensions were contained in small glass capillaries. In the emission spectrum measurements, we employ an InGaAs diode array that suffers from a number of dead pixels (due to an earlier inadvertent overexposure), which we blank out, hence some spectra reveal an apparent hole that has no scientific meaning.

4.2.2 Quantum dot nanoparticles

We study PbS nanoparticle quantum dots, the emission wavelengths of which are compatible with silicon nanophotonic crystals, that is, the emission wavelength is longer than the Si band gap absorption edge at 1100 nm. The nanoparticles were obtained in aqueous suspension from Suzhou Xingshuo Nanotech Co., Ltd. (Mesolight). From the peak of the emission spectrum measured with the dots in the original suspension at $9560 \pm 60 \text{ cm}^{-1}$, we estimated the average quantum dot diameter to be $D_{\text{size}} = 3.47 \pm 0.09 \text{ nm}$, using the calibration of Moreels *et al.* [165]. The inorganic lead sulfide core of the quantum dots is covered by a poly(ethylene glycol)-amine ligand that is used to couple to a PGMA polymer layer on the silicon substrate and eventually onto silicon photonic crystals (using polymer brush layers), see Ref. [161].

In Figure 4.3 the black data represent PbS-OA QDots from Evident Technologies in toluene (times 4.34), red data are PbS-OA QDots from M K Impex Corp. (MKNano) in toluene (times 1.02), green data are PbS-PEG-NH₂ QDots from Suzhou Xingshuo Nanotech Co., Ltd. (Mesolight) in water (times 4.03), blue data are PbS-OA QDots from STREM Chemicals, Inc. (CANdots) in toluene (times 1.64), magenta data are PbS-PEG-NH₂ QDots from Suzhou Xingshuo Nanotech Co., Ltd. (Mesolight) in chloroform.

4.3 Results and discussion

4.3.1 Emission spectra and nanocrystal dimensions

We present in Figure 4.3 the continuous-wave (cw) emission spectra obtained from all different quantum dot suspensions. We observe a broad spectral distribution for each of the quantum dot suspensions compared to quantum dots that emit within visible wavelengths (FWHM 12-42) [168], but within acceptable values (FWHM 100-160) compared to near-infrared emitting PbS quantum

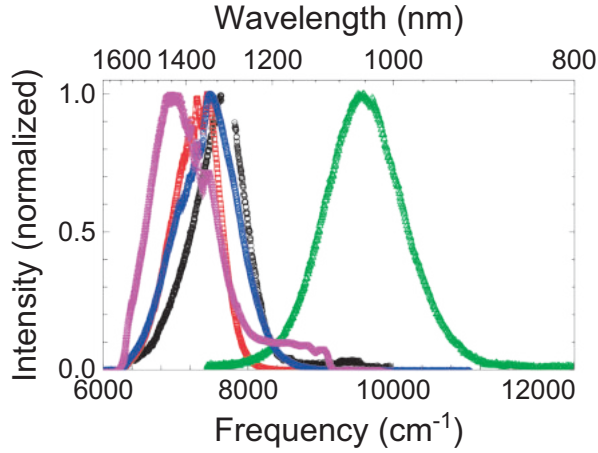


Figure 4.3: Scaled emission spectra measured for all quantum dot suspensions, bottom abscissa gives wavenumbers and the top one wavelengths. Black data are for QDot sample B, red data for sample E, green data for sample D, blue data are for sample A, and magenta data are for sample C.

dots [169]. The spectral width is attributed to the size distribution of the quantum dots, due to the statistical nature of the liquid synthesis following the pioneering work of Murray *et al.* [170]. Table 4.1 lists emission peak wavelengths λ_{max} , emission peak wavenumbers $\tilde{\nu}_{max}$, full width at half maximum (FWHM), that are all in the range of silicon transparency, and also cover several telecom bands [171].

Table 4.1: Properties of the quantum dots studied in this chapter. The column "QD" gives the alpha numbering of the quantum dot suspensions, column "label" the abbreviation of the sample name, column " λ_{max} " the wavelength at maximum intensity, column "FWHM" the wavelength range for the full width at half maximum, column " $\Delta\lambda/\lambda$ " the relative bandwidth, column " $\tilde{\nu}_{max}$ " the frequency at maximum intensity and column "QD diameter" the diameter range of the quantum dots where the range corresponds to the FWHM.

QD	label	λ_{max}	FWHM	$\Delta\lambda/\lambda$	$\tilde{\nu}_{max}$	QD diameter
A	CANdots	1336 nm	172 nm	12.9%	7486 cm ⁻¹	3.82-6.19 nm
B	Evident	1301 nm	136 nm	10.5%	7684 cm ⁻¹	3.96-6.15 nm
C	MesoCl	1421 nm	210 nm	14.8%	7037 cm ⁻¹	4.14-6.19 nm
D	MesoH ₂ O	1051 nm	133 nm	12.7%	9514 cm ⁻¹	2.81-4.46 nm
E	MKNano	1345 nm	138 nm	10.3%	7434 cm ⁻¹	4.15-6.17 nm

From the emission spectra, we infer the quantum dot diameters and the concomitant size distribution, starting from the sizing curve of Moreels *et al.* [165]. Whereas Moreels *et al.* used the optical absorption peak to estimate the exciton energy, we use here the peak in the emission spectrum to gauge the exciton.

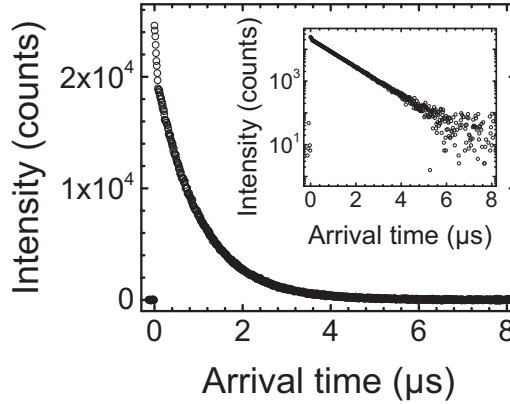


Figure 4.4: Luminescence decay curve from PbS quantum dots (sample A) at 7463 cm^{-1} ($\lambda = 1340\text{ nm}$) near the emission peak. Background-corrected counts are shown *versus* photon arrival time. Inset: the same data on a semi-logarithmic plot.

Therefore, to reasonably invoke the Moreels *et al.* sizing curve, we must assume that the Stokes shift is small. Indeed, this assumption is validated by the discussion of Husken [172] on similar PbSe nanocrystals that reveal a shift of a few **10s** meV, hence only a few % of the exciton energy.

The nanocrystal size distributions listed in Table 4.1 are conservatively estimated as the ranges where the emission intensities have dropped to 5% of the peak intensities. In the evaluation of the Mesolight quantum dots in chloroform (sample C), we propose to neglect the unusual square shoulder in the range between 8330 and 9150 cm^{-1} ($\lambda = 1093\text{-}1200\text{ nm}$), and assume that the “true” exciton spectrum ends around $\tilde{\nu} = 8330\text{ cm}^{-1}$ ($\lambda = 1200\text{ nm}$). Since all studied nanocrystal samples have diameters $D_{\text{size}} \leq 6.2\text{ nm}$, we conclude that all quantum dot samples easily fit within the pores of our 3D silicon inverse woodpile photonic crystals that have diameters in excess of $D_{\text{pore}} \geq 150\text{ nm}$, hence it should be readily feasible to dope such photonic crystals with these quantum dots, which is confirmed by our successful results [155, 161].

4.3.2 Time-resolved emission

Figure 4.4 shows a typical decay curve of lead sulfide quantum dots with an OA capping suspended in toluene. The decay curve is nearly single-exponential, which means physically that all nanocrystals emit photons with the same total rate Γ_{tot} that is equal to the sum of radiative Γ_{rad} and non-radiative Γ_{nonrad} rates: $\Gamma_{\text{tot}} = \Gamma_{\text{rad}} + \Gamma_{\text{nonrad}}$. While either or both the radiative and the non-radiative rates may be distributed, it seems very unlikely that a distribution of radiative rates would exactly cancel a distribution of non-radiative rates to yield a total decay rate with a narrow distribution.

To interpret emission rates from time-resolved decay curves (as in Fig. 4.4), proper care must be taken of the modeling procedure, see, *e.g.*, Refs. [35, 173]

(notably the supplementary). Figure 4.5(a) shows an example of a nearly exponential decay curve, that is readily modeled with a textbook single-exponential model, yielding a total emission rate $\Gamma_{\text{tot}}^s = 1.017 \mu\text{s}^{-1}$. The residuals, shown in the lower panel, are distributed around zero, which is a second indication that the single-exponential is a reliable model. Thirdly, the goodness-of-fit, expressed as a reduced χ_{red}^2 [174], is equal to $\chi_{\text{red}}^2 = 1.02$, close to the ideal value $\chi_{\text{red}}^2 = 1$ which indicates that the data are reliably described by the single-exponential decay model. Hence, at this emission wavenumber, all OA-covered quantum dots in toluene in sample A have closely the same excited-state lifetime.

Figure 4.5(b) shows an example of a decay curve from PEG-NH₂-capped PbS quantum dots suspended in water that markedly deviates from exponential decay. The data differ from the single-exponential model notably at short and at long arrival times. Indeed, the residuals for the single-exponential model are systematically non-zero at short arrival times below $0.5 \mu\text{s}^{-1}$, but also in the whole time domain, indicative of a non-matching model. Thirdly, the goodness-of-fit is equal to $\chi_{\text{red}}^2 = 2.45$ which differs markedly from 1. Physically, such a non-exponential decay curve means that the quantum dots likely have a distribution of total rates Γ_{tot} , as a result of a distribution of non-radiative rates Γ_{nonrad} [173].¹

Since non-exponential decay is often observed with quantum dot nanocrystals [175–178], much work has been done to practically model a physically significant distribution of decay rates to a decay curve [173, 179, 180]. A time-resolved decay histogram is described as

$$I(t) = I(0) \int_{\Gamma=0}^{\infty} \phi(\Gamma) e^{-\Gamma_{\text{tot}} t} d\Gamma, \quad (4.1)$$

where $\phi(\Gamma)$ represents a probability distribution of single-exponential decays over total decay rates Γ with dimension of inverse decay rate. A particularly successful probability distribution is a log-normal distribution of total decay rates $\phi(\Gamma)$, in other words, a Gaussian plotted on a logarithmic abscissa [173, 179]:

$$\phi(\Gamma) = A \cdot \exp \left[- \left(\frac{\ln \Gamma - \ln \Gamma_{\text{mf}}}{w} \right)^2 \right], \quad (4.2)$$

where A is a normalization constant, Γ_{mf} the most frequent decay rate (see Fig. 4.6), and w is a dimensionless width parameter that determines the distribution width at $\frac{1}{e}$. The width parameter w is related to the distribution width $\Delta\Gamma$ as follows:

$$\Delta\Gamma = 2\Gamma_{\text{mf}} \sinh(w). \quad (4.3)$$

Since the amplitude A , the most frequent rate constant Γ_{mf} , and w are adjustable parameters, there is only one additional adjustable parameter compared to a single-exponential model. While the model is heuristic (“it fits well with few parameters”) the log-normal shape has several rationales, namely that a nanocrystal size distribution is typically also log-normal (or Schulz distribution) [181],

¹We can safely exclude the possibility that the *radiative* rates are distributed, since the quantum dots are located in a homogeneous dielectric medium with a constant local density of optical states [5].

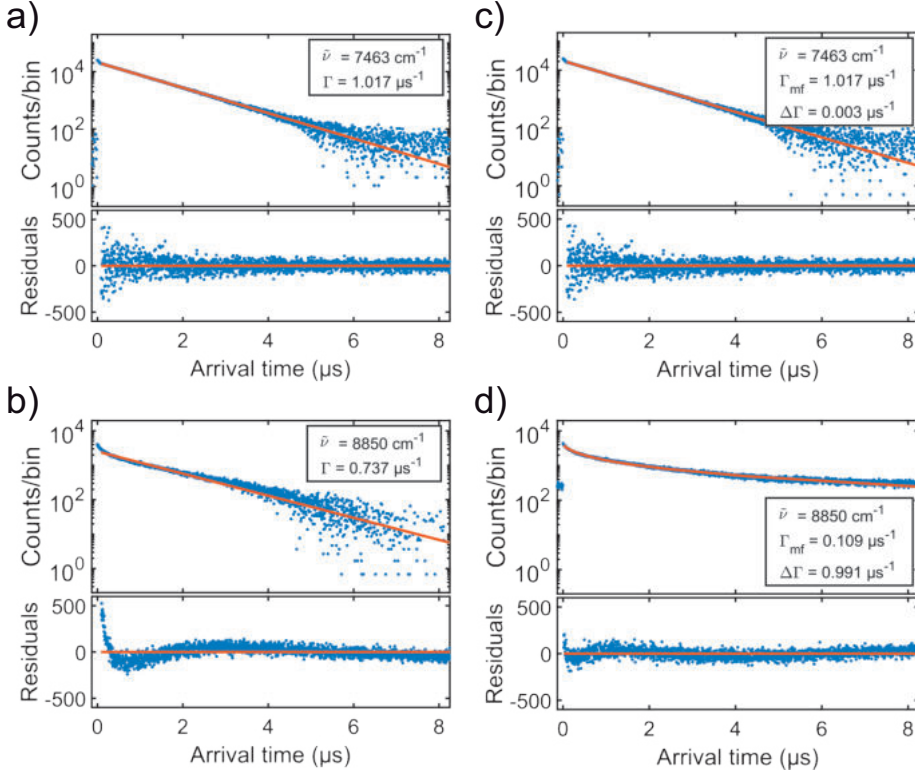


Figure 4.5: Examples of decay histograms fitted with a single-exponential (a+b) and log-normal (c+d) model. The legends list the decay rate of the single-exponential or the log-normal model and the lower panels show the residuals between data and model. (a) Histogram for sample A at $\tilde{\nu} = 7463 \text{ cm}^{-1}$ ($\lambda = 1340 \text{ nm}$) that agrees well with a single-exponential decay model since the residuals are randomly distributed about zero. (b) Histogram for sample D at $\tilde{\nu} = 8850 \text{ cm}^{-1}$ ($\lambda = 1130 \text{ nm}$) that differs markedly from single-exponential decay since the residuals systematically deviate from zero. (c) Histogram for sample A at $\tilde{\nu} = 7463 \text{ cm}^{-1}$ ($\lambda = 1340 \text{ nm}$) that agrees well with a log-normal decay model since the residuals are randomly distributed about zero. (d) Histogram for sample D at $\tilde{\nu} = 8850 \text{ cm}^{-1}$ ($\lambda = 1130 \text{ nm}$) that differs slightly from a log-normal decay since the residuals deviate from zero.

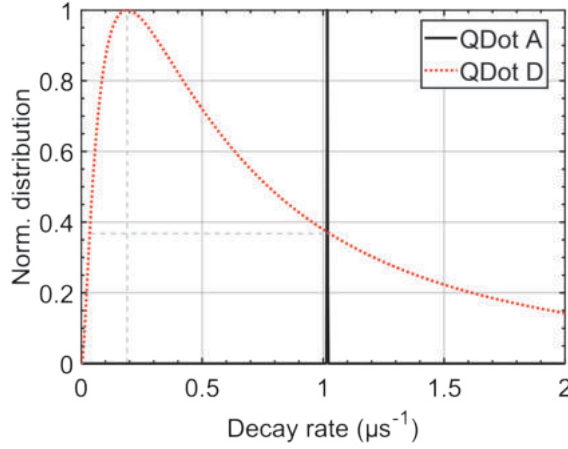


Figure 4.6: Examples of log-normal distributions of decay rates $\sigma(\Gamma_{\text{tot}})$. The dotted red curve is for parameters $\Gamma_{\text{mf}} = 0.109$ and $\Delta\Gamma = 0.991$ from Fig. 4.5(d), and the black curve is for parameters $\Gamma_{\text{mf}} = 1.017$ and $\Delta\Gamma = 0.003$ from Fig. 4.5(c).

the log-normal distribution only allows positive rates as it should physically be.² Since a log-normal model has only one more adjustable parameter compared to a single-exponential decay model, it is numerically stable.

In Figures 4.5(c+d), we show the same two exemplary decay histogram as in Figures 4.5(a+b), now compared to log-normal models. The quantum dots of sample D reveal a clear non-exponential decay, that is much better modeled with the log-normal distribution. Indeed, the goodness-of-fit equals $\chi_{\text{red}}^2 = 1.32$, much closer to 1 than for the single-exponential model ($\chi_{\text{red}}^2 = 2.45$). The resulting most-frequent decay rate is $\Gamma_{\text{mf}} = 0.109 \mu\text{s}^{-1}$ and the width is $\Delta\Gamma = 0.991 \mu\text{s}^{-1}$, hence the width is much greater than the most frequent rate ($\Delta\Gamma > \Gamma_{\text{mf}}$), characteristic of a broad distribution of total rates, see Figure 4.6. From the log-normal model for the nearly-exponentially decaying CANdots, we obtain a decay rate $\Gamma_{\text{mf}} = 1.017 \mu\text{s}^{-1}$ with a goodness-of-fit $\chi_{\text{red}}^2 = 1.0191$. The width is $\Delta\Gamma = 0.003 \mu\text{s}^{-1}$, much less than the most frequency decay rate, typical of a narrow distribution, as shown in Figure 4.6. The advantage of a log-normal model is that it successfully models both nearly-exponential and strongly non-exponential decay curves emitted by all different quantum dots with different cappings in different suspending media studied in this chapter.

²Other popular models are Gaussian or Lorentzian distributions of total rates. These models have the disadvantage that they consider nonphysical negative decay rates. To remedy this issue, one is then tempted to cut the distribution below zero rate, but this brings about the disadvantages that the distribution is not analytical anymore, and furthermore the proper normalization of the distribution becomes complicated [173].

4.3.3 Emission rate *versus* frequency and size

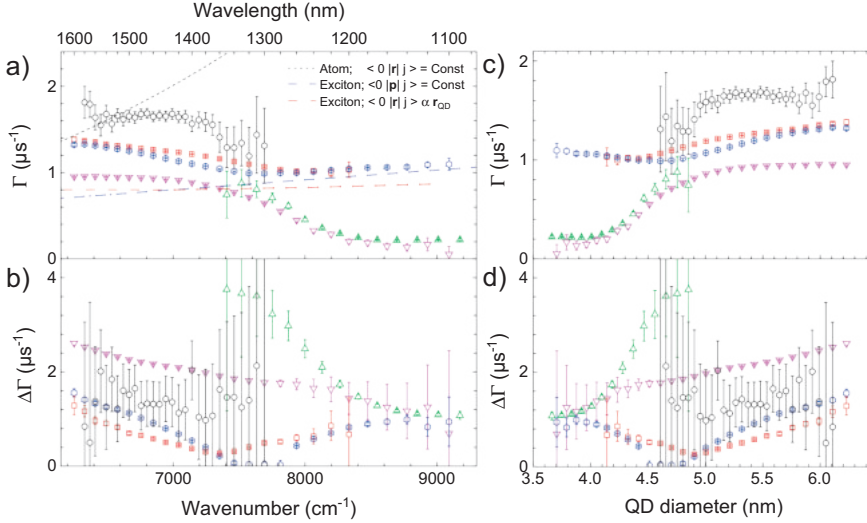


Figure 4.7: (a+b) Measured decay rates for all quantum dot suspensions *versus* wavenumber (bottom abscissa) or wavelength (top abscissa). (a) Most-frequent decay rates Γ_{mf} from the log-normal model, black circles represent sample B (OA, toluene), red squares sample E (OA, toluene), green triangles sample D (PEG, water), blue hexagons sample A (OA, toluene), and magenta inverted triangles sample C (PEG, chloroform). The black dotted line represents a model of an atomic dipole, the blue dashed-dotted line an ideal two-level-exciton with constant transition dipole, and the red dashed curve an ideal two-level-exciton with transition dipole proportional to quantum dot diameter. (b) Logarithmic widths of the distribution $\Delta\Gamma$ from the log-normal model, symbols same as in (a). (c+d) Measured quantum dot decay rates *versus* quantum dot (QDot) diameter, obtained from modeling the decay curves with a log-normal model. (c) Most frequent decay rate Γ_{mf} , (d) logarithmic width of the distribution $\Delta\Gamma$ derived from fitting with lognormal.

Figure 4.7(a) shows the decay rate Γ *versus* both wavenumber (bottom abscissa) and wavelength (top abscissa), specifically the most frequent decay rate Γ_{mf} obtained from the log-normal models. If we first zoom in on the OA-capped quantum dots suspended in toluene (samples A, B, E), we see that overall the decay rate is fairly constant with frequency over a broad range from 6200 to 9100 cm^{-1} . In detail, at low frequency below 7500 cm^{-1} there is a mildly decreasing trend and above 8000 cm^{-1} a slightly increasing trend, but in view of sample-to-sample variations and other sources of uncertainty it is not certain that these trends are significant. The PEG-capped quantum dots (samples C, D) also show a constant (or slightly decreasing) trend around 1 μs^{-1} up to about 7200 cm^{-1} . But with further increasing frequency the emission rate changes dramatically, decreasing by nearly 5-fold to about 0.2 μs^{-1} up to about 8500 cm^{-1} and remaining constant at higher frequency.

Figure 4.7(b) shows the logarithmic widths of the decay rate distributions $\Delta\Gamma$ versus wavenumber (bottom abscissa) and wavelength (top abscissa). First concentrating on the OA-capped quantum dots suspended in toluene (samples A, B, E), the widths start at $\Delta\Gamma = 1.2$ to $1.6 \mu\text{s}^{-1}$, decrease with frequency up to 7300 cm^{-1} (sample E) or 7500 cm^{-1} (A) (close to the spectral maxima (see Table 4.1)) to nearly vanishing width, characteristic of single-exponential decay. Subsequently, the widths slightly increase to about $\Delta\Gamma = 1.0 \mu\text{s}^{-1}$. For sample B, the widths vary between $\Delta\Gamma = 1$ and $2 \mu\text{s}^{-1}$ with a relatively large uncertainty so it is not reasonable to assign a trend. The PEG-capped quantum dots (samples C, D) show monotonously decreasing trends over the whole accessible frequency ranges, ranging from $\Delta\Gamma = 2.5$ to $1.6 \mu\text{s}^{-1}$ (sample C) or from $\Delta\Gamma = 3.8$ to $1.1 \mu\text{s}^{-1}$ (sample D). Overall, it is also clear that all OA-capped quantum dots have (much) narrower decay distributions than the PEG-capped quantum dots.

4.3.4 Discussion: sharply decreasing emission rates with PEG surface groups

We have seen above in Figure 4.7(a) that quantum dots with PEG capping have a dramatically different trend (above 8000 cm^{-1}) than the ones capped with oleic acid. Let us briefly discuss five possible reasons for this striking difference. First and foremost, it is from the onset remarkable that the major trend is a *decrease* of the emission rate, since this emission rate represents a total emission rate that is equal to a sum of radiative and non-radiative rates. Therefore, the occurrence of any of the common quenching mechanisms (e.g. charge transfer, energy transfer, see Ref. [182]) may safely be excluded since all of them result in an increase of the non-radiative rate, which is in contradiction with the observations.

A second hypothesis is to look for a physico-chemical reason of the suspending liquid, notably the polarity of the solvent. We may safely reject this hypothesis, since the dramatic decrease happens both for QDots suspended in water (polar) and chloroform (apolar).

A third hypothesis is whether there is a resonance in the suspending liquid that might "siphon off" the excitation from the quantum dot, so as to reduce the total emission rate. Apart from the problem that this hypothesis corresponds to an increased total emission rate, a major problem with this hypothesis is that there are no known strong resonances above 8000 cm^{-1} in both water and chloroform, since vibrational resonances are below 3600 cm^{-1} (the famous O-H stretch in water) and electronic resonances are above 25000 cm^{-1} ; put differently, both water and chloroform are completely transparent in the relevant range above 8000 cm^{-1} .

A fourth hypothesis is whether in the PEG-covered QDots an acoustic (surface) mode is excited by the presence of the excited electron-hole pair, as reported before on thin films and nanoparticles [183–185], where THz-range oscillations were reported. This hypothesis also does not match with our observations since the resonance frequencies of acoustic oscillations are a factor of at least 20-fold too low compared to the relevant range above 8000 cm^{-1} .

Since the hypotheses discarded above are naturally related to the frequency

of light, we now discuss quantum dot diameter as possible determining factor. Therefore, we plot in Figures 4.7(c,d) the same data as in Figures 4.7(a+b), but now *versus* quantum dot diameter, as obtained from the emission frequency using the sizing curve of Moreels *et al.* [165] mentioned above. For the OA-capped PbS quantum dots in toluene, we observe in Fig. 4.7(c) a slight decrease of the most frequent rate Γ_{mf} with increasing diameter, followed by a slight increase above $D_{size} = 4.5$ nm diameter. For both PEG-capped PbS quantum dots in both water and chloroform, we see that the most frequent rate Γ_{mf} increases markedly in a remarkable S-like shape centered at about $D_{size} = 4.5$ nm diameter.

In the diameter representation, another hypothesis could be that either the electron or hole - part of the excited exciton - become somehow trapped in the PEG surface group, for instance, due to the presence of the oxygen ions. This hypothesis could make sense, since the reduced emission rate occurs for smaller quantum dots, so that the likelihood of one of the charges traveling to the surface is reasonably greater than for larger quantum dots; on the other hand, a difficulty with this hypothesis is that it is unclear why a nanocrystal diameter $D_{size} = 4.5$ nm would then be a critical value. Taken together, we currently summarize that we have no convincing rationale for the dramatic change in the emission rate of PEG-covered quantum dots.

4.3.5 Models of frequency-dependent decay rates

To interpret the broadband frequency-dependent decay rates of the PbS quantum dot nanocrystals, we look back at Figure 4.7(a), where we restrict this discussion to the relative simple behavior of the OA-capped quantum dots suspended in toluene, and compare the measurements to several different theoretical models.

First, let us consider a quantum-mechanical oscillator typical of a two-level atomic emitter [186], since quantum dots were originally advertised to be “solid-state atoms” [187], and since this model was employed in early nanophotonic work [159]. In a homogeneous dielectric medium with refractive index n_m , the radiative emission rate Γ_{at} as a function of (angular) frequency ω is equal to

$$\Gamma_{at}(\omega) = \frac{\omega^3 n_m \mu_{if}^2}{3\pi \epsilon_0 \hbar c^3} \quad (4.4)$$

with μ_{if} the transition dipole moment, ϵ_0 the dielectric permittivity of free space, $\hbar$ the reduced Planck’s constant, c the speed of light in free space. The resulting curve, assuming a refractive index $n_m = 1.4338$ for toluene, and a transition dipole moment equal to $|\mu_{if}| = 3.6$ D [188], is plotted in Figure 4.7(a). The model does not agree with the data since its trend is much too steep. Therefore, we conclude that PbS quantum dots as quantum emitters are not behaving like artificial atoms, in matching the original warning in Ref. [187].

As a second model, we consider the radiative emission rate from a single exciton Γ_{ex} (excited electron-hole pair) to the ground state where the particles have recombined. Following Refs. [189] the rate is equal to

$$\Gamma_{ex}(\omega) = \frac{ne^2 F^2}{3\pi \epsilon_0 m^2 \hbar c^3} \omega |\langle 0 | \mathbf{p} | j \rangle|^2 \quad (4.5)$$

with e the electron charge, F a local field factor (of order unity), m the electron rest mass, and $|\langle 0|\mathbf{p}|j\rangle|$ the transition dipole moment in momentum $\mathbf{p}$ space (instead of position $\mathbf{r}$ space). Assuming that interband transitions are mostly determined by the Bloch functions in the unit cell, the momentum-space transition dipole moment is *independent* of the nanocrystal diameter or the emission frequency, hence the decay rate of an ideal two-level exciton is linearly proportional to the emission frequency, as predicted in earlier work [190]. The rate of the ideal two-level exciton model is shown in Figure 4.7(a), where we take $|\langle 0|\mathbf{p}|j\rangle| = 3.6$ D from theoretical work of Liu *et al.* [188]. The model agrees better with our observations than the dipolar atomic model, in particular, the ideal two-level exciton model agrees very well at frequencies above 7600 cm^{-1} both in the magnitude and in the trend. At frequencies below 7600 cm^{-1} the model agrees less well with the data, notably since the data reveal a *decreasing* trend that is opposite to the *increasing* trend of the model. Nevertheless, the transition dipole moment of 3.6 D gives a good agreement with the observations (assuming all measured decay to be radiative), which means that the transition dipole of PbS nanocrystal quantum dots is substantial as it is greater than, e.g., CdSe nanocrystal quantum dots [191].

As a third model, also shown in Figure 4.7(a), we heuristically modify the ideal two-level exciton model by assuming the transition dipole moment (in momentum space) not to be constant, but that the magnitude of the dipole moment is proportional to the radius of the nanocrystals $|\langle 0|\mathbf{p}|j\rangle| \propto (D_{\text{size}}/2)$. Since we can only assume a proportionality, we have to fix the offset, which we choose (somewhat arbitrarily) at 7000 cm^{-1} . It is clear that the trend of this model is in better overall agreement than the ideal two-level model, but it also does not explain the slightly downward trend in the observations over the whole range from 6200 to 9200 cm^{-1} . Therefore, more theoretical work is called for to model the size and frequency-dependent emission rate of PbS nanocrystal quantum dots.

To place our observations in perspective, we review previous observations on different quantum dots, both nanocrystalline and self-assembled ones. Van Driel *et al.* studied CdSe and CdTe nanocrystal quantum dots in suspension and observed markedly increasing trends of the total decay rate Γ_{tot} with frequency [189, 192], which was successfully described by the thermal occupation of dark exciton states at room temperature that give rise to a strong decrease of the emission rate, and a supra-linear trend that matched well with tight-binding calculations. Walters *et al.* studied Si nanocrystals fabricated by ion implantation at a variable distance to a reflector to distinguish radiative from non-radiative decay (by the Drexhage effect [5, 193]) and reported a radiative rate Γ_{rad} that increases with frequency [194]. Johansen *et al.* studied self-assembled InAs quantum dots made by molecular beam epitaxy (MBE) by the Drexhage effect and reported that the radiative rate Γ_{rad} slightly decreases with increasing frequency, which was successfully explained by a decreasing oscillator strength with decreasing quantum dot size, due to a concomitant decreasing overlap of the electron and hole wave functions [195]. Leistikow *et al.* studied CdSe quantum dots by the Drexhage effect and observed that the radiative rate Γ_{rad} first increases and then decreases with increasing frequency [191]. Thus, the trends in Figure 4.7(a) for

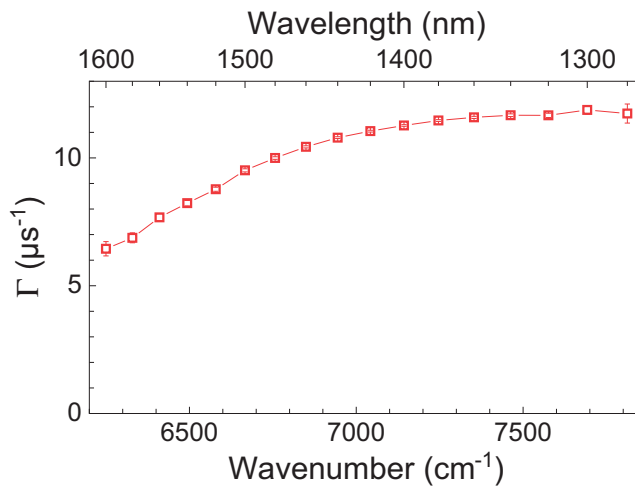


Figure 4.8: Frequency dependent excited-state lifetime measurements of sample E quantum dots dip-coated on a clean silicon bar. The decay rates are plotted *versus* wavenumber (bottom abscissa) and wavelength (top abscissa).

OA-capped quantum dots in toluene are similar to those for self-assembled InAs quantum dots. In contrast, the strongly varying decay rates of the PEG-capped quantum dots differ strikingly from all earlier observations reviewed above.

4.3.6 Quantum dots on a silicon surface

Figure 4.8 shows the frequency-dependent emission rates of lead sulfide quantum dots dip-coated on a flat silicon surface. We observe an increase of the decay rates with increasing wavenumber which is expected from our ideal two-level-exciton model. For the dip-coating procedure we used MKNano PbS-OA quantum dots (red) from Figure 4.7. The decay rates increased from $\approx 1.1 \mu\text{s}^{-1}$ to $\approx 10 \mu\text{s}^{-1}$. The increase can be attributed to the environmental changes of the quantum dots being close to a bulk semiconductor.

4.4 Summary and outlook

We present broadband spectra and excited-state lifetimes of lead sulfide quantum dots with different surface groups (oleic acid (OA) and polyethylene glycol (PEG)) suspended in polar and apolar liquids. The time-dependent emission revealed both exponential and non-exponential decay traces, and all were successfully modeled with a log-normal distribution of decay rates. For OA-covered QDots we find that the most frequent decay rate is nearly constant with frequency, whereas the PEG-covered QDots reveal a remarkable downturn starting at 8000 cm^{-1} (wavelength $\lambda = 1250 \text{ nm}$) or conversely for nanocrystal diameters less than 4.4 nm . We compare our experimental data to several theoretical

models. An atomic point dipole does not at all match with the data, an ideal two-level-exciton model gives a reasonable description, which slightly improves if we assume the transition dipole moment to scale linearly with the QDot diameter. For the remarkable PEG-QDot downturn we have discussed five possible hypotheses - namely quenching in general, solvent polarity, generic resonances, acoustic (surface) modes, exciton or charge trapping - none of which convincingly explains the observations, thus calling for future studies including theory or simulations. On a dip-coated silicon substrate, we observe an increase of the decay rate with frequency which agrees with expectations from the literature. The knowledge assembled in this chapter is relevant to understand the optical properties of lead sulfide quantum dots attached to a polymer layer in- and outside silicon photonic crystals.

CHAPTER 5

Polymer brush layers on 3D silicon-air interfaces

We present a versatile method to coat structured silicon-air interfaces with polymer brushes. Such a method is required for the fabrication of organic thin film-functionalized 3D nanostructures. We show the successful fabrication of structured silicon test substrates made by nanoimprint lithography (NIL) and additionally use 2D and 3D photonic crystals. Deep reactive ion etching (DRIE) has been used to etch nanopores into the silicon. In this process, the protection gas leads to the deposition of inert fluorocarbon layers on the silicon-air interface that hamper a polymer brush deposition. We discuss the crucial cleaning steps to ensure that the substrate has a clean silicon surface. We show initial results, based on contact angle measurements, that 3D silicon photonic band gap structures can be successfully functionalized with brush layers.

5.1 Introduction

Control over the interaction between light and matter has far-reaching consequences in chemistry, materials science, physics, and biology. An important tool for the advanced control of light is offered by 3D photonic crystals with a photonic band gap, a range of frequencies for which light is forbidden to exist by interference [19, 196]. The fabrication of spatially periodic nanostructures to achieve a 3D photonic band gap is of great interest in the field of Nanophotonics [17, 197]. The opportunity to modify the 3D nanostructure by means of surface chemistry would open up the possibility to introduce additional elements and molecules to the system.

The local density of optical states (LDOS) and spontaneous emission of quantum emitters (such as quantum dot nanocrystals) depend not only on the emission frequency but also on the position of the emitters [14, 15]. Therefore it is a challenge for chemistry to place emitters at well-defined positions inside a 3D photonic crystal.

Polymer brushes can be suitable candidates to position nanoparticles. Brushes are a form of surface-bound polymer grafts that possess chains in a stretched conformation in good solvents due to molecular crowding [63]. To the ends or to the side-chains of the individual polymer chains one can covalently attach an emitting nanoparticle with the complementary functional group, which is thus

positioned relative to the substrate by the polymer chain. Combinations of 3D nanolithography and polymer brush technology with nanometer length control can therefore be expected to yield the desired precision over emitter positioning.

Since 3D photonic band gap crystals require high quality structures, silicon is a suitable material because one can profit from many available silicon nanofabrication methods [198]. Moreover, silicon has the required high refractive index for band gap formation. Therefore the "challenge for chemistry" narrows down to silicon. In Chapter 2 it was shown that polymer brushes were placed on silicon substrates [199] by silanization and atom transfer radical polymerization (ATRP) [200].

In the nanofabrication of 3D silicon photonic crystals, one often employs deep reactive ion etching [201] based on the Bosch process [202]. In one of the two main steps (the so-called protection step), a deposition of fluorocarbons takes place. Fluorocarbon layers on silicon are "show stoppers" for sensitive surface chemistry such as ATRP. We quickly encountered that the presence of fluorocarbons on silicon nanostructures is a wider problem in nanotechnology that merited much more of our attention.

Here, we show the functionalization of 2D and 3D silicon nanostructures and test structures with polymer brush layers, with the aim to solve the issue of fluorocarbon deposition and to study the brush layer formation inside nanoporous structures and at their edges. Poly(glycidyl methacrylate) (PGMA) was chosen as a polymer brush for controlling the quantum dot position due to the fact the polymer kinetics can be well controlled [145, 203]. We focus in this chapter on how to remove fluorocarbon layers from structured silicon with a combination of wet cleanings step and a thermal treatment to oxidize and remove remaining fluorocarbons. We explore how to grow polymer brushes on micro/nano-structured silicon surfaces made by nanoimprint lithography. Additionally, 2D and 3D nanostructured silicon photonic crystal structures are used as substrates for brush layer formation.

5.2 Materials and methods

In Table 5.1 we show an overview of the four types of silicon samples studied in this chapter that are discussed below.

Table 5.1: List of samples studied.

Sample name in the text	Sample name in the lab	Remarks
2DPC	EasyCleave sample 1	Silicon wafer piece with arrays of 2D nanopores [204, 205].
3DPC	PG-EBAR-30032017-CH4B	Silicon bar with 14 photonic crystals ($6 \times 3D$, $8 \times 2D$) fabricated with the single-step etch mask process described in Ref.[206, 207].
NIL1	Nanoimprint lithography sample 1	Silicon sample with trenches with a depth of 100 nm, a width of 130 nm and a period of 400 nm.
TB1	Test bar 1	Silicon bar made from a silicon wafer ($0.5 \text{ mm} \times 0.5 \text{ mm} \times 10 \text{ mm}$).
TW1	Test wafer 1	Silicon wafer coated with a 1940 nm thick fluorocarbon layer.
TW2	Test wafer 2	Silicon wafer coated with a 4350 nm thick fluorocarbon layer.

5.2.1 Materials

Acetone (Biosolve, 99.5%) and 2-propanol (Biosolve, 99.5%) were used for the cleaning steps in the ultrasonication bath. Anisole (Sigma-Aldrich, $\geq 99\%$) and poly(methyl methacrylate) (PMMA, 350 kD, Sigma-Aldrich) were used for the resist layer. Aqueous hydrofluoric acid (50 wt%) and potassium hydroxide (25 wt%) were used as received from Fischer Scientific. The ceric ammonium nitrate-based chromium etchant (10.9 wt% water, 4.25 wt% ceric ammonium nitrate, 84.85% perchloric acid, chrome etch no1, VLSI, Techni France), hydrochloric acid (HCl, 36 wt%, VLSI, BASF), and hydrogen peroxide (H_2O_2 , 31 wt%, VLSI, BASF), all as aqueous solutions, were used as received. Nitric acid (100%, KMG Ultra Pure Chemicals) for the pre-furnace cleaning was used in very large scale integration (VLSI) quality with an impurity metal ion concentration per element of 10 to 50 ppb, and a particle concentration $< 250/\text{mL}$. Nitric acid (69% in water, VLSI, BASF) for the pre-furnace cleaning was used as received. Sulfuric acid (H_2SO_4 , 95-97%) for the piranha solution was received from Sigma-Aldrich. Glycidyl methacrylate (GMA, 97%, Sigma-Aldrich) was filtered over basic aluminum oxide to remove the inhibitor monomethyl ether hydroquinone. Copper(I) chloride (CuCl , Sigma-Aldrich, 97%) was purified by stirring in glacial acetic acid (Sigma-Aldrich, $\geq 99.5\%$), filtering, and washing with ethanol (Biosolve, 96%)

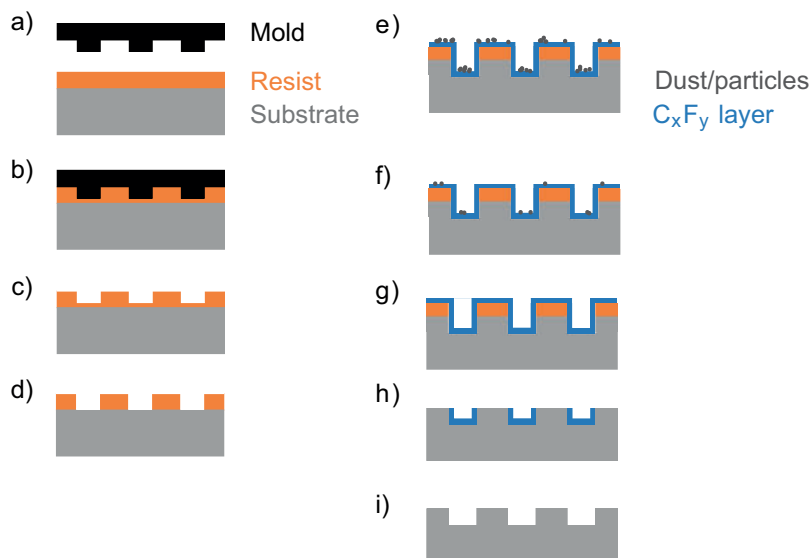


Figure 5.1: Scheme of nanoimprint lithography: a) A polymer resist film (orange) has been spincoated on the silicon substrate (grey) and a mold (black) with the desired pattern has been created, b) the mold has been pressed at high pressure (130 bar) into the resist, c) the mold has been removed leaving the pattern in the resist, d) the residual polymer layer has been removed with an oxygen plasma, e) the pattern has been etched into the silicon by RIE. A fluorocarbon layer (blue) has been formed on top of the silicon originating from the protection step of the Bosch process, f) the sample has been cleaned in acetone in the ultrasonication bath, g) the sample has been cleaned in isopropanol in the ultrasonication bath, h) the resist has been removed by oxygen plasma cleaning, i) the organic residues like fluorocarbons have been removed by piranha solution.

three times. The catalyst was dried under vacuum at room temperature for 48 h. Copper(II) bromide (CuBr_2 , Sigma-Aldrich, $\geq 99\%$), methanol (Biosolve, 99.8%), 2,2-bipyridyl (BiPy, Sigma-Aldrich, 99%), 2-bromo-2-methylpropionic acid allyl ester (Sigma-Aldrich, 98%), hexachloroplatinic acid (Sigma-Aldrich, 99.9%) and dimethylchlorosilane (Sigma-Aldrich, 98%) were used as received. Millipore milli-q grade (resistivity $> 18 \text{ M}\Omega\text{cm}$) water was used in the experiments.

5.2.2 Silicon sample fabrication

Nanoimprint lithography

To fabricate corrugated silicon surfaces we used nanoimprint lithography (NIL) [208]. The steps for the NIL process are shown in Figure 5.1. In the first step a silicon $\langle 100 \rangle$ wafer (100 mm diameter, single side polished, p-type) was coated with a resist layer. Therefore the wafer was cleaned with piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (30 wt%), 3:1 v/v) for 15 min, and extensively rinsed with wa-

ter. *Caution: Piranha solution reacts violently with many organic materials and should be handled with great care!* The cleaned wafer was then spincoated with 6 wt% PMMA (350 kD in anisole) at 500 rpm for 5 s, and then the spincoater was set to 3000 rpm for 30 s, see Figure 5.1(a). The silicon wafer was diced into small silicon wafer pieces. The nanoimprint mold was cleaned by ultrasonication in acetone and the contact angle was measured to be 113° . The cleaned mold was pressed into the resist with a pressure of 130 bar at 180°C for 5 min, see Figure 5.1(b). The mold was removed (Figure 5.1(c)) and the resist residues where the mold was in contact with the substrate were removed with oxygen plasma cleaning (NL-CLR-Tetske, standard cleaning recipe, 10°C , 10 mTorr, 20 sccm O_2 , 20 W, 100 s), see Figure 5.1(d)).

RIE of nanoimprint samples

With reactive ion etching the structure was etched into the silicon (NL-CLR-Tetske, 10°C , 10 mTorr, 25 sccm CHF_3 , 5 sccm O_2 , 60 W, etch rate for silicon 15–25 nm/min), see Figure 5.1(e) with the NIL mask. The substrate was cleaned with acetone (Figure 5.1(f)) and isopropanol using ultrasonication for 10 min each to remove organic residues (Figure 5.1(g)). The substrate was dried in a nitrogen stream. To remove the resist the substrate was cleaned in oxygen plasma for 30 min (Figure 5.1(h)). As a final cleaning step the substrate was cleaned with piranha solution for 15 min to remove organic residues and fluorocarbons (Figure 5.1(i)).

2D silicon photonic crystal samples

All etching experiments for 2D and 3D silicon photonic crystals were performed using a SPTS Pegasus reactive ion etcher in the MESA+ Nanolab using C_4F_8 as the protection gas, SF_6 as the etching gas and O_2 for plasma cleaning to remove leftover fluorocarbons from the sample surface after etching. So-called Easy-cleave samples that are 2D photonic crystals were studied which are described by Woldering [205]. The samples have 7 different fields with pore diameters between 200 and 500 nm.

Silicon test wafers covered with fluorocarbons

In the same etching machine (SPTS Pegasus) that was used for the fabrication of the silicon photonic crystals, two test wafers were covered with fluorocarbons by increasing the duration of the protection steps with fluorocarbons. It was done in such a way to ensure that the chemical composition of the fluorocarbons was the same as for the etched samples. On one wafer we deposited 3 cycles of 5 min duration with deposition steps of 100 s and etching steps of 0.1 s (TW1), on the second 5 cycles of 8.5 min duration (TW2).

Silicon bar samples

The silicon bar samples were used as a test sample for the cleaning procedure and for the fabrication of 3D silicon photonic crystal samples. An etch mask was made from silicon nitride with the desired sample specifications. Figure 5.3 shows an overview of the silicon bar characteristics.

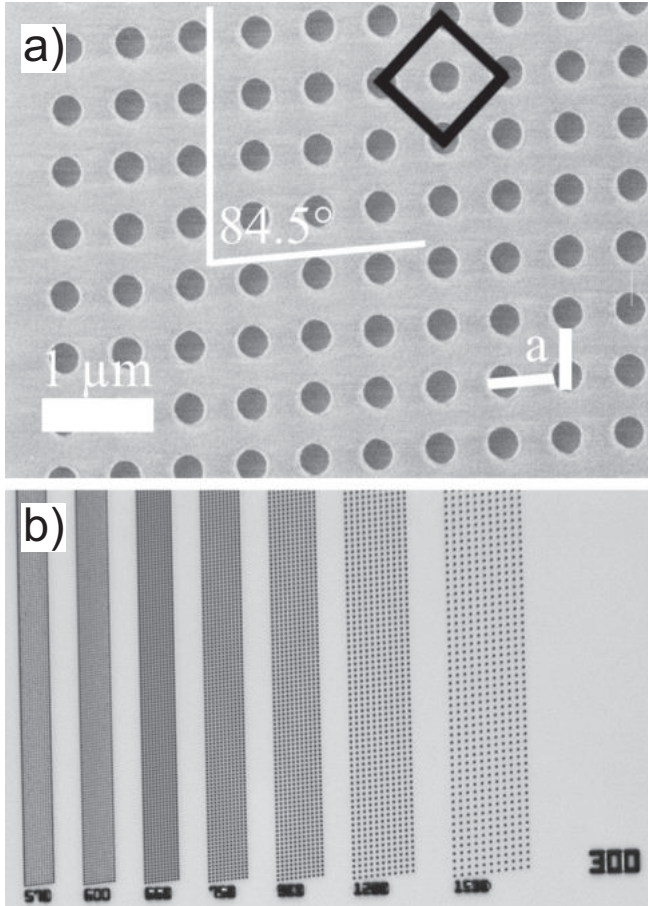


Figure 5.2: SEM image taken from Woldering [205] of an 2D silicon photonic crystal sample (Easycleave sample): a) The positions of the pores are orientated in a centered rectangular lattice. The outline is shown in black. The angle of the two axes (shown in white) to each other is 84.5° . The shortest distance between the pores is indicated with a , b) There are seven periodic 2D photonic crystal fields and six different sets of diameter to pore distance combinations. Here the set for the diameter of 300 nm is shown. The distance between the pores is varying from $a = 570$ nm to 1500 nm.

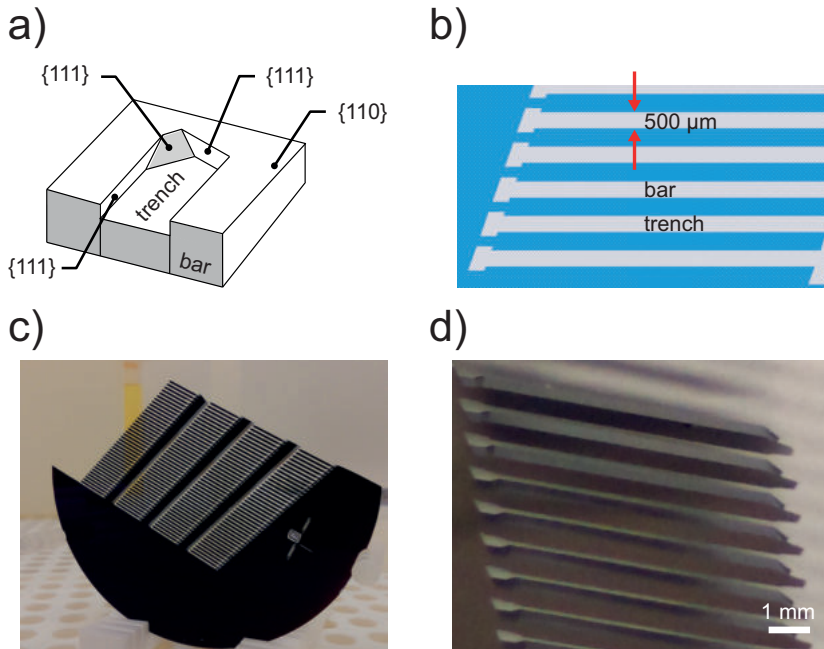


Figure 5.3: Fabrication details of the silicon bar samples: a) Scheme of the crystal orientations of the silicon wafer. At the locations of the trenches the silicon was etched. The remaining silicon constitutes the silicon bars, b) top view of the etch mask, c) image of the whole silicon wafer from which the silicon bar samples have been fabricated, d) zoom-in image of eight silicon bars on the wafer. The scale bar represents 1 mm.

The etching performed done in aqueous potassium hydroxide (KOH, 25 wt%) at 75 °C for 500 min to ensure the silicon is completely etched away. Figure 5.4 shows a silicon bar sample which was broken off from the wafer. The wafer containing the silicon bars was cleaned in hydrofluoric acid (50 wt%) to remove the silicon nitride etch mask.

Fabrication and coating of 3D silicon photonic crystals samples

For silicon photonic crystal samples (with 2D and 3D photonic crystal structures) a silicon bar was used on which the crystals were etched. A detailed fabrication description can be found in the thesis of Grishina [206]. Starting from a small piece of a single crystalline silicon wafer a 50 nm thick chromium layer spotted (NL-CLR-Sputterke) on two adjacent planes of the wafer piece. The masks of the pore locations of the photonic crystals were patterned with focused ion beam (FEI Nova 600 Nanolab FIB, Ga source FIB) under 45° angle with respect to the gallium ion beam gun. After the edge mask was created, the pores were etched into the silicon by deep reactive ion etching (SPTS Pegasus DRIE etcher, using SF₆ as etching gas). Since the etching of the two perpendicular sets of pores was performed consecutively, one after another we cleaned the silicon bar after

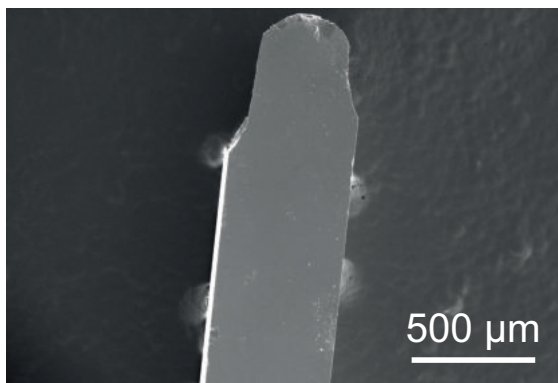


Figure 5.4: SEM image of a silicon bar sample TB1. The scale bar represents 500 μm .

the etching of the first side from most of the fluorocarbons by oxygen plasma (standard oxygen plasma cleaning procedure, SPTS Pegasus). The second side of the silicon bar was etched and cleaned with oxygen plasma to result in the 3D silicon photonic crystal sample.

Contact angle measurements were done on the silicon bars with the etched pores after the fabrication and cleaning. Sample 3DPC was additionally cleaned with piranha solution to activate the surface for ATRP. Figure 5.5 shows three contact angle measurements. The contact angle of the monolayer is presented in Figure 5.6. The successful coating with a PGMA polymer brush layer results in the contact angles presented in Figure 5.7.

5.2.3 Cleaning

Chromium etching

The chromium hard mask of about 50 nm thickness was removed with a chromium etchant solution, namely a ceric ammonium nitrate-based etchant that exhibits an etch rate of 60 nm/min. To ensure that the chromium was removed completely, the sample was kept in the etchant for 60 s. The sample was intensively rinsed for 1 h with deionized (DI) water to ensure most of the perchloric acid, and the cerium-salts to be removed. The sample was dried in a nitrogen stream.

RCA-2 cleaning protocol

RCA-2 cleaning was used to remove metal residues from the samples [209].¹ A glass beaker with a volume of 3 L was placed on a hot plate. 1500 mL DI water and a stirring bar were added. The magnetic stirrer was turned on and 300 mL of hydrochloric acid was slowly added. The solution was heated to 70 °C (setpoint: 80 °C). When the solution reached 70 °C, 300 mL hydrogen peroxide was slowly added under stirring. Once the solution reached 70 °C again the samples were

¹RCA-2 was developed in 1965 by Werner Kern while working for RCA, the Radio Corporation of America.

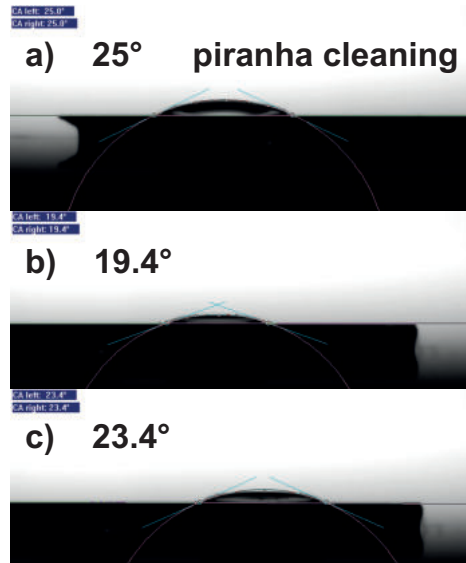


Figure 5.5: Contact angle measurements on silicon bar sample 3DPC with photonic crystal structures cleaned with piranha solution: a) Contact angle on the top part of the silicon bar, b) contact angle on the middle part of the silicon bar, c) contact angle on the bottom part of the silicon bar.

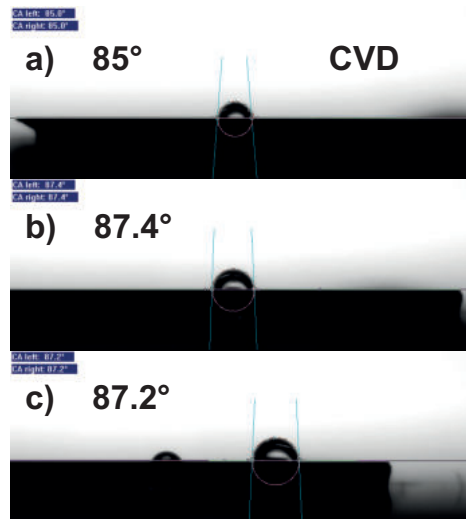


Figure 5.6: Contact angle measurements on silicon bar sample 3DPC after chemical vapor deposition (CVD) of ATRP initiator: a) Contact angle on the top part of the silicon bar, b) contact angle on the middle part of the silicon bar, c) contact angle on the bottom part of the silicon bar.

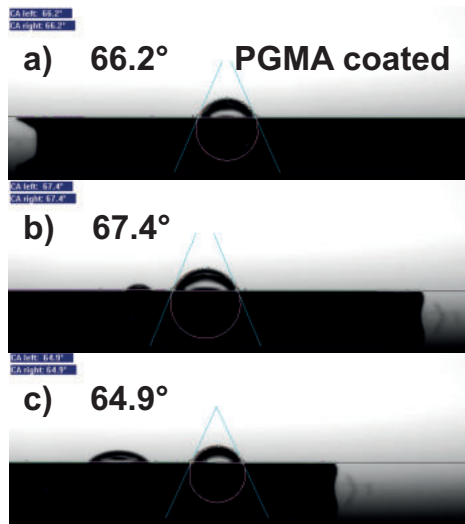


Figure 5.7: Contact angle measurements on silicon bar sample 3DPC after coating of the PGMA layer: a) Contact angle on the top part of the silicon bar, b) contact angle on the middle part of the silicon bar, c) contact angle on the bottom part of the silicon bar.

added with the help of a suitable holder. The samples were kept in the RCA-2 solution for 15 min. After 15 min the samples were rinsed in a water bath with "recipe 2" of the "quick dump rinser" (QDR). With recipe 2 we ensured that the water was slowly replaced inside the bath in a continuous flow with a minimized risk to lose the sample. The rinsing was repeated until the resistivity value ($> 10 \text{ M}\Omega\text{cm}$) was reached indicating an acid free environment.

Pre-furnace cleaning in nitric acid

Organic traces were removed by placing the sample into a bath of HNO_3 (99%, room temperature) for 10 min. The sample was transferred to a second bath under the same conditions and was cleaned for another 10 min. The sample was rinsed with DI water and dried under a nitrogen flow. The dried sample was then transferred into a closed beaker of boiling HNO_3 (69% in water, 95°C) and was cleaned for 10 min. The sample was rinsed with DI water and was dried under a nitrogen stream. In addition photonic crystal nanostructures were placed into a clean beaker which was closed with a cap and was kept at 45°C on a hot plate to ensure that no water was present inside the pores before the furnace cleaning.

Sample holder for silicon bars

For all cleaning steps mentioned above a home-made holder was used to ensure a successful cleaning of the silicon bar samples. Figure 5.8 shows the first prototype of the holder. One silicon bar is placed in the middle of the three available positions. The top part is adjustable to fix the silicon bar in place.

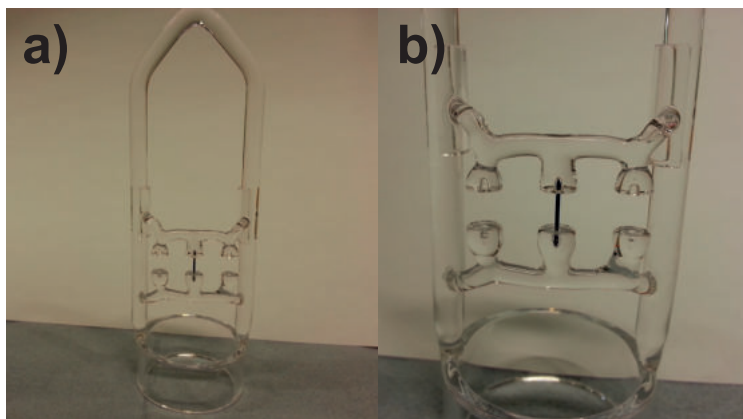


Figure 5.8: Sample holder used for cleaning the silicon bars in the clean room: a) Sample holder for silicon bars. b) close-up of the silicon bar ($0.5 \times 0.5 \times 8$ mm) placed in the middle position of the holder.

Furnace treatment

To ensure removal of the last residues of fluorocarbons, the 2D and 3D silicon samples were thermally treated in a furnace at $800\text{ }^{\circ}\text{C}$ under 100% O_2 for 90 min to oxidize and remove the remaining fluorocarbons from the pore surface inside the silicon. Figure 5.9 shows the sample holder horizontally placed on a dummy wafer. The silicon bars samples are located as indicated by the red arrows.

5.2.4 Polymer brush synthesis

ATRP initiator (vapor-phase) deposition

The silicon substrates were cut into small pieces of 2.5×2.5 cm, cleaned with piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$, 3:1 v/v) for 30 min, and extensively rinsed with water and ethanol. The substrates were dried in a nitrogen stream. ATRP initiator ($30\text{ }\mu\text{L}$) was placed onto a small plastic petri dish at the bottom of a desiccator and the cleaned substrates were placed around it. The desiccator was evacuated by a vacuum pump for 10 min. Vapor-deposition was allowed to proceed for 16 h. Afterwards the substrates were sonicated in toluene for 1 min, washed with ethanol, water and acetone, and dried in a nitrogen stream. The characterization of the ATRP initiator monolayer is described in the method section of Chapter 2.

ATRP procedure to graft PGMA brushes

GMA (16.05 g, 0.11 mol) monomer and BiPy (423 mg, 2.7 mmol) were added to a mixture of water (3 mL) and methanol (12 mL). The solution was purged with argon for 30 min under continuous stirring. CuCl and CuBr_2 were added to another flask and flushed with argon for 15 min. The monomer solution was transferred by a previously flushed syringe to the catalyst flask. The resulting polymerization

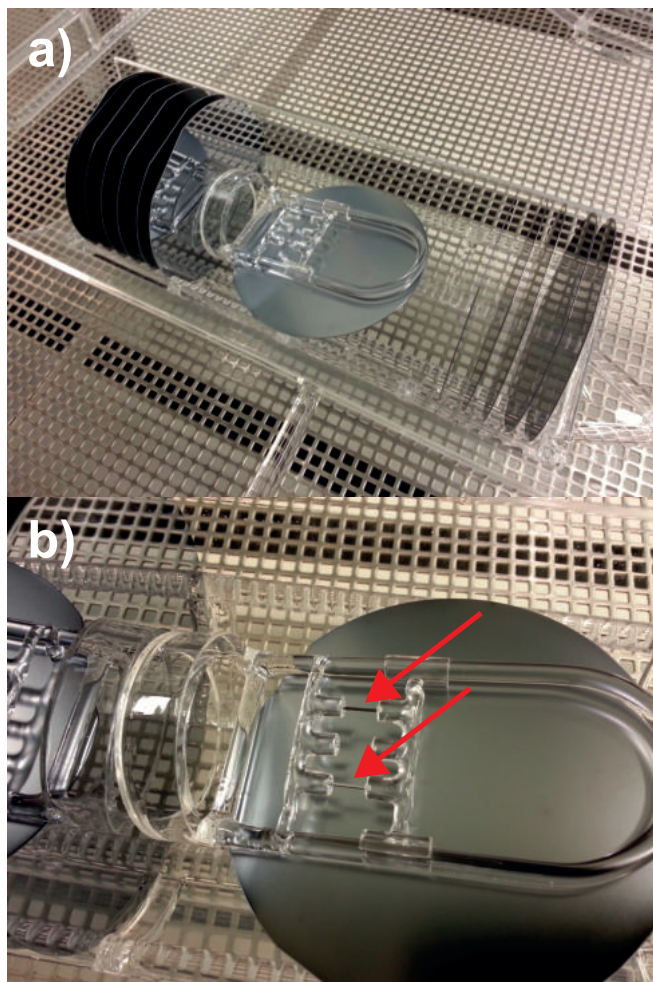


Figure 5.9: Sample holder used for removing the fluorocarbons in the furnace: a) Sample holder placed onto a wafer boat which is moved into the furnace, b) close-up of the holder which is placed on a dummy wafer. The holder is placed against a vertically placed dummy wafer to guarantee a stable position on the wafer boat.

solution was stirred for an additional 30 min under argon while stirring. Afterwards the solution was transferred by a previously flushed syringe to the reaction flasks containing the substrates. The polymerization was allowed to proceed for 60 min. After the polymerization was done the substrates were cleaned extensively with Milli-Q water, ethanol, and acetone to remove non-reacted monomer, metal-complex, and remaining catalyst residues. The substrates were dried in a nitrogen stream to obtain the samples with the thin poly(glycidyl methacrylate) polymer brush film.

5.2.5 Characterization

Scanning electron microscopy and energy-dispersive X-ray spectroscopy

High resolution scanning electron microscopy (SEM) images were taken with an acceleration voltage tuned between 1-2 kV (Zeiss MERLIN HR-SEM, Oberkochen, Germany). The SEM was equipped with an energy-dispersive X-ray spectroscopy (EDX) unit. The spatial resolution for EDX is down to nanometer range and applicable for elements heavier than boron in the periodic system.

All other SEM images were taken with a FEI Sirion HR-SEM. The SEM has a hot field emission gun. The minimum operating voltage is 200 V, the maximum operating voltage is 30 kV. The probe current can be adjusted between 0.7 pA and 10 nA. The resolution is 1.5 nm for 15 kV @ 9 pA and 2.5 nm for 1 kV @ 0.7 pA. The magnification ranges between 20 and 10^6 times.

Contact Angle measurements

Static contact angles of a 4 μL water sessile drop were measured on flat 2D silicon substrates (OCA15, Dataphysics, Germany). For the silicon bars contact angles were measured using a water droplet with a volume below 0.5 μL . The contact angles were manually fitted. The measurement error was estimated to be on the order of 10%.

Ellipsometry

The dry thickness of the fluorocarbon layers was measured using a variable-angle spectroscopic ellipsometer at three different incident angles 65°, 70°, and 75° at room temperature (Woollam M-200UI ellipsometer, LOT Oriel GmbH, Darmstadt, Germany). The thickness was determined through the analysis of a three-layer (Si/SiO₂/fluorocarbon) with known thicknesses and refractive indices of Si and SiO₂ and an assumed refractive index of 1.42 for the fluorocarbon layer using commercial software (WVASE32, LOT Oriel GmbH, Darmstadt, Germany).

5.3 Results and discussion

As described in the Introduction above, a good quality brush layer can only be formed if fluorinated residues from the Bosch etching process can be removed completely. That is the reason why we started with test wafers that had a fluorinated layer to test if it is possible to remove the fluorocarbons from the

surface by wet chemical cleaning steps. By using a thick fluorocarbon layer to start with, it was easier to determine a change in thickness of the fluorinated layers. After that we used corrugated surfaces made by NIL, and then went on to 2D and 3D photonic crystals.

Table 5.2 shows the cleaning steps needed to receive clean silicon samples. The optimal cleaning procedure was found to consist of several cleaning steps in wet chemicals and a furnace treatment. In steps 1-3 the chromium hard mask was removed from the silicon samples by a chromium etchant solution and by rinsing with water. In steps 4-6 the organic residues and by-products from the chromium etchant were removed by RCA-2. During steps 7-14 the samples were prepared for the furnace treatment which was used to oxidize the fluorocarbons. Any metal or organic contamination was removed by several cleaning steps in nitric acid. The furnace treatment took place in steps 15-16. For 2D and 3D silicon photonic crystal samples the remaining fluorocarbons were oxidized at 100% O₂ at 800 °C in the furnace for 90 min to be able to clean them from the pore surface.

Table 5.2: Steps for cleaning the silicon surface before surface chemistry can be applied.

step number	name of cleaning step
Removal of chromium	
1	Chromium etching
2	rinsing with water
3	drying in nitrogen stream
Removal of contaminations (from 1-3)	
4	RCA-2 cleaning
5	long rinsing with water
6	drying in nitrogen stream
Removal of organic and inorganic residues	
7	HNO ₃ 99% (A)
8	HNO ₃ 99% (B)
9	rinsing with water
10	drying in nitrogen stream
11	HNO ₃ 69% , 95 °C (A)
12	HNO ₃ 69% , 95 °C (B)
13	long rinsing with water
14	drying in nitrogen stream
Removal of fluorocarbons from pores	
15	additional drying in a beaker heated to 45 °C
16	furnace treatment at 800 °C (100% oxygen)

5.3.1 Fabrication and cleaning of flat silicon wafers

The first tests of the cleaning procedure were done on a flat silicon wafer coated with fluorocarbons. The wafer was coated with a thick fluorocarbon layer to make it easier to characterize the remaining layer thickness with contact angle measurements and with ellipsometry. The fluorocarbon layer was made with long protection steps in the DRIE etcher using C_4F_8 gas and by keeping the etching steps short. This way the fluorocarbon thickness increased with time. The thickness of the fluorocarbon layers derived from 3 measurements each was 1940 ± 146 nm (3 deposition cycles, wafer TW1) and 4350 ± 464 nm (5 deposition cycles, wafer TW2).

For the test wafers TW1 and TW2 we first used HNO_3 (69% in water, 95 °C) cleaning which had no effect on the thick fluorocarbon layer. Then RCA-2 cleaning was performed on the TW1 sample (steps 4-6). Only for the test wafers it was done in this order. No fluorocarbons could be determined anymore by ellipsometry after the RCA-2 cleaning (steps 4-6). This suggests that the fluorocarbon layer was completely removed from the wafer. To verify the ellipsometry measurements, the test wafer TW1 was characterized by contact angle measurements. Before cleaning we observed that the water droplet did not wet the surface. The contact angle was $111.7^\circ \pm 0.9$. After the cleaning we observed a hydrophilic silicon surface on which the water droplet spread in all directions. The contact angle was lowered to $9.9^\circ \pm 0.4$.

5.3.2 Fabrication and cleaning of 2D silicon photonic crystal samples

The next step was to verify if the cleaning procedure is applicable to 2D photonic crystal samples of pores in silicon. A detailed description of the so-called Easy-cleave samples is given in the methods section of this chapter and can be found in the thesis of Woldering [205]. Basically, a 2D silicon photonic crystal sample consists of seven different fields of pores with a fixed diameter with varying the distance of the pores to each other. The etch mask was made from chromium and the etching was done in a deep reactive ion etcher (SPTS Pegasus). Figure 5.10(a) shows a SEM image of two neighboring pores from a sample that was treated with chromium etchant solution to remove the hard mask of chromium from the silicon surface (steps 1-3). The scallops coming from the individual Bosch etching steps are visible. Apparent clean pores are visible. Figure 5.10(c) shows the result of the SEM analysis after cleaning step 6. New contaminations as spots are apparent in the pores and on top of the substrate which have been introduced with the chromium etchant. Possible contaminations are cerium- and chromium-based salts from the wet etching step. This result shows that although we intensively rinsed the samples to get rid of most contaminations, an additional cleaning step is required to remove particles. Subsequently the sample was treated with RCA-2 (Table 5.2, steps 4-6). Figure 5.10(c) shows a clean top surface of the silicon and the pores appear much cleaner. In Figures 5.10(b+d) we present the results from electron backscattering (EBS). Figure 5.10(d) shows

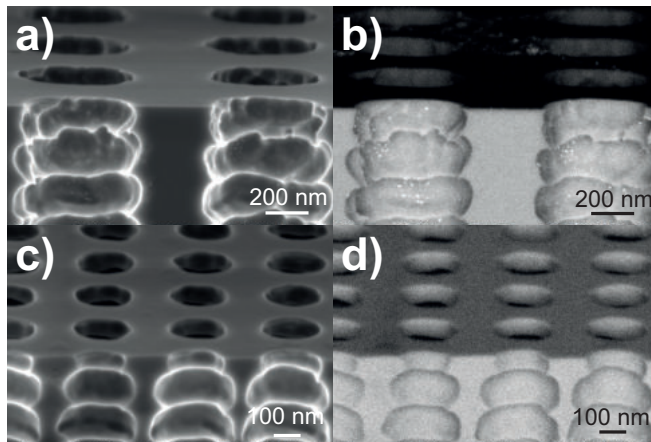


Figure 5.10: High resolution SEM images of the sample 2DPC. The wafer surface is seen above. a) SEM image of two cleaved pores after cleaning step 3. b) SEM-EBS image of two cleaved pores using a detector for elements with a high atomic mass. The chromium layer that was used as a hard mask was removed with a chromium etchant solution. c) SEM image of four cleaved pores after cleaning step 6. d) SEM-EBS image of four cleaved pores.

that the pores are much cleaner concerning heavy elements compared to Figure 5.10(b). At this point we are sure that we have successfully removed the chromium hard mask and the resulting contamination of cerium salts.

The next challenging task was to ensure the fluorocarbons are removed from inside the photonic crystal pores (steps 7-16). Following later in the discussion, we show that the cleaning step for oxidizing the fluorocarbons inside the pores of silicon is needed. Initially, these additional cleaning steps were excessive to be on the safe side to ensure there are no fluorocarbons remaining. By comparing the carbon amount before and after the furnace treatment the success of this treatment can be assessed. Since carbon is part of the polymer residue of the fluorocarbons, its presence/absence can indicate if the cleaning step improved the sample quality. To remove the residues of fluorocarbons we cleaned the 2D silicon photonic crystal in nitric acid (99%) at room temperature (Table 5.2 up to step 10) and in hot nitric acid (95 °C, 69%), see Table 5.2 up to step 14. Afterwards the sample was oxidized at 800 °C to remove the fluorocarbons from the pores (step 16). Figure 5.11 shows one of the samples after the furnace treatment.

Table 5.3: Results of the EDX measurements on 2D silicon. The atom percentage for each element is shown before and after each fabrication step.

element	atom% after Cr etchant and RCA-2	atom% after furnace	atom% after PGMA coating
Aluminum	3.8 ± 0.3	0.7 ± 0.1	0.5 ± 0.1
Carbon	12.9 ± 0.9	4.1 ± 0.5	13.7 ± 0.4
Oxygen	4.1 ± 0.3	6.6 ± 0.2	10.5 ± 0.2
Silicon	79.1 ± 0.9	88.6 ± 0.5	75.3 ± 0.4

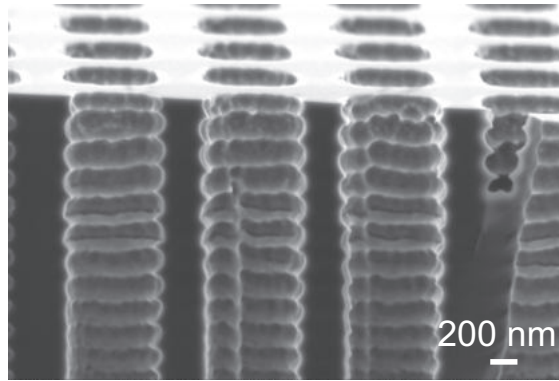


Figure 5.11: SEM image of the sample 2DPC after heating for 90 minutes at 800 °C under 100% oxygen to clean the substrate from fluorocarbons (step 16).

A clean silicon surface and clean pores are observed but the presence of fluorocarbons left in the pores cannot be assessed by this image. To verify the success of the cleaning procedure the pores were analyzed with energy-dispersive X-ray microanalysis (EDX). In Table 5.3 the atom percentages for carbon, oxygen and silicon are shown at different steps in the cleaning procedure. Atom percentages for fluorine which is highly characteristic for the fluorocarbons are not presented in Table 5.3 since the amount of F was below the detection sensitivity of EDX. After the removal of the chromium hard mask from the silicon and the RCA-2 cleaning step an atom percentage of carbon of 12.9 atom% was observed. The atom percentage of silicon was 79.1 atom%. After the furnace treatment at 800 °C an atom percentage of carbon of 4.1 atom% was found. This shows that a 3-fold decrease of the carbon amount present in the pores was achieved. If we assume that most of the carbon contamination was removed in previous cleaning steps like RCA-2 and nitric acid, we can conclude that most of the remaining carbon amount arises from the polymer layer of fluorocarbons. Due to the successful cleaning of the bar the silicon percentage was increased to 88.6 atom%.

X-ray photoelectron spectroscopy (XPS) was measured on the 2D silicon crystal samples to be able to detect fluorine with a higher sensitivity than EDX. Nevertheless the results obtained from these measurements were not conclusive either since it was not possible to detect signal deep inside the bulk silicon where

the pores of the 2D crystals are located. XPS is in this way more useful to measure monolayers or flat samples but it is less suitable for the silicon photonic crystal samples. A large intensity for fluorine on the surface of the silicon sample was found. The large intensity originated from scattered electrons. It was not possible to trace back the origin of the signal for fluorine due to the scattering. The resolution decreased therefore below the specifications of the instrument making this method not useful for our research.

In conclusion, the silicon surface was well cleaned after the furnace step such that surface chemistry was possible to be applied.

5.3.3 Fabrication and cleaning of 3D silicon photonic crystal samples

The final challenging step was to apply the developed cleaning procedure to silicon bars with 3D photonic crystals. Detailed sample specifications are given in the methods section. For the fabrication of 3D silicon photonic crystals a chromium etch mask was used. The locations and the diameter of the pores were written into the chromium mask by focused ion beam. The pores were etched with deep reactive ion etching into the silicon. Many different structures were fabricated on a single silicon bar and not all details are presented here. A typical pore diameter of a 3D silicon photonic crystal was 320 nm (the real diameter might differ due to limitations of the etching precision). The pore depth was measured to be around 5 μm depending on which set of pores was analyzed by X-ray tomography which can be found in the thesis of Grishina [206] and in Chapter 6 by X-ray fluorescence tomography. Here an additional handling challenge arose: Since the available equipment in the cleanroom is optimized for silicon wafers, we had to develop a glass holder for the silicon bar during the cleaning steps. Figure 5.8 shows the holder that was used for every cleaning step such that the samples did not have to be removed which would have caused risk of loss, contamination or damage to the silicon bar. For the final cleaning step, the furnace treatment, the holder went into the furnace being placed horizontally on a carrier wafer. Figure 5.9 shows the holder that was fixed by pushing the bottom part against a dummy wafer which was placed vertically on the furnace boat. The front and the back of the wafer boat were protected by multiple wafers to make sure the gas flow was homogeneous and the samples were in a protected environment. The samples were heated at 100% oxygen to oxidize the fluorocarbons. A duration of 90 min was chosen to minimize the formation of silicon oxide [210]. If the silicon oxide layer would grow too thick the pore diameter of the 3D photonic crystal structures could be compromised. At this point we decided to not introduce another cleaning step to remove the silicon oxide layer with hydrofluoric acid (HF). It was estimated that after 90 min the oxide layer thickness would increase by 7.5 nm which is acceptable for our aim [211, 212]. Before surface chemistry was applied, the silicon oxide layer was hydroxylated in piranha solution to form silanol groups on the surface.

To confirm that the removal of chromium and the following RCA-2 cleaning step was successful in combination with the sample holder, EDX was measured

Table 5.4: Results of the EDX measurements on silicon test bar. The atom% for each element is shown before and after the cleaning procedure.

element	atom% before cleaning	atom% after all cleaning steps
Carbon	28.49 ± 0.03	9.06 ± 0.02
Oxygen	2.23 ± 0.03	not detected
Silicon	63.66 ± 0.18	90.94 ± 0.20
Chromium	5.62 ± 0.21	not detected

before and after the cleaning (see Table 5.4). Before chromium removal a Cr atom percentage of 5.62 atom% and a C atom percentage of 28.49 atom% were observed. After the cleaning with chromium etchant and RCA-2, the chromium percentage was reduced to below the detection limit of EDX. Any possible metal residues which would be still on the bar were removed in the pre-furnace cleaning step with HNO_3 . The carbon contamination was 3-fold lower to reach an atom percentage of 9.06 atom% which is in good agreement with the results of cleaning a 2D photonic crystal sample. In conclusion, these results show that the cleaning procedure was successful for silicon wafers, silicon wafers with 2D photonic crystals and for silicon bar samples with 3D photonic crystal structures.

5.3.4 Grafting of polymer brushes on corrugated silicon surfaces

To test the polymerization procedure described in Chapter 2 on cleaned structured silicon substrates corrugated silicon surfaces were fabricated by nanoimprint lithography. The aim was to coat these structured silicon-air interfaces with thin polymer brush layers as an intermediate step before grafting polymer brushes into the pores of the 2D and 3D photonic crystals. The steps on silicon with sharp edges (90° and 270°) are intended to mimic the 3D network structure of a photonic crystal. Moreover the sample geometry allows to inspect the brush layer from above, and to study how the thickness of the polymer brush layer varies along the corrugated surface.

Figure 5.12(a) shows a SEM image of the resist layer on sample NIL1 that was patterned with the mold. Areas on the substrate were observed which had a thicker layer than others. The areas with thicker layers were rough, the areas in between the thicker layers were smooth. This observation indicated that the resist layer was too thin and/or the imprint step was too short. Both would result in an incomplete filling such that the underlying silicon is not entirely covered by the resist. The fabrication was not further improved at this stage since the sample quality was sufficient to perform coating tests of the sample surface with a monolayer and with polymer brushes.

The mold created lines in the resist layer leaving resist residues behind at the imprinted areas. Figure 5.12(a) shows the result corresponding to the fabrication step presented in Figure 5.1(c). Figure 5.12(b) shows a SEM image after the residual resist was removed by oxygen plasma and the uncovered silicon surface was etched. Figure 5.12(b) corresponds to the fabrication step shown in Figure 5.1(e). The dark material on top of the silicon was the remaining resist that

protected the silicon at the areas which should not be etched. The lines were roughly 100 nm in height, the thicker silicon lines were 130 nm wide, and the pitch was 400 nm. Unfortunately the line height could not be accurately determined from the SEM images. Figure 5.12(b) shows that the corners were not accurately etched, *i.e.*, the angle between the etched part and the side walls of the Si lines deviated from 90°. An angle of $99^\circ \pm 3^\circ$ was obtained from the SEM images. The silicon lines were quite rough on the side walls. One possible explanation is that the PMMA was already etched at some locations, such that the deep reactive ion etching occurred through these holes in the PMMA lines. Figure 5.12(c) shows sample NIL1 after the resist was removed by ultrasonication in acetone and isopropanol (Figure 5.1(f-g)). The sample was additionally cleaned with piranha solution. The sample did not seem to be fully clean, which was surprising after cleaning with piranha solution. Particles were observed where the silicon was etched; therefore the sample was cleaned one more time in an ultrasonication bath in acetone and isopropanol before the polymerization procedure was performed. The silicon lines were rough on top and at the side walls. Figure 5.12(d) shows the substrate after coating with a thin layer of PGMA. The main conclusion is that corrugated silicon surfaces can be cleaned from fluorocarbons so that surface chemistry is feasible. This will help to understand how a polymer layer will look like inside the pores.

Figure 5.12 presents the substrate from a different perspective to monitor the roughness and width of the silicon lines. Figure 5.12(e) shows the substrate before the polymerization and f) shows the corrugated surfaces coated with PGMA. The silicon was obviously covered with a thin polymer layer as witnessed by the smoothening of the sharp features which were apparent in Figure 5.12(e). In conclusion, the corrugated silicon samples were successfully fabricated and the surface was coated with a polymer brush layer.

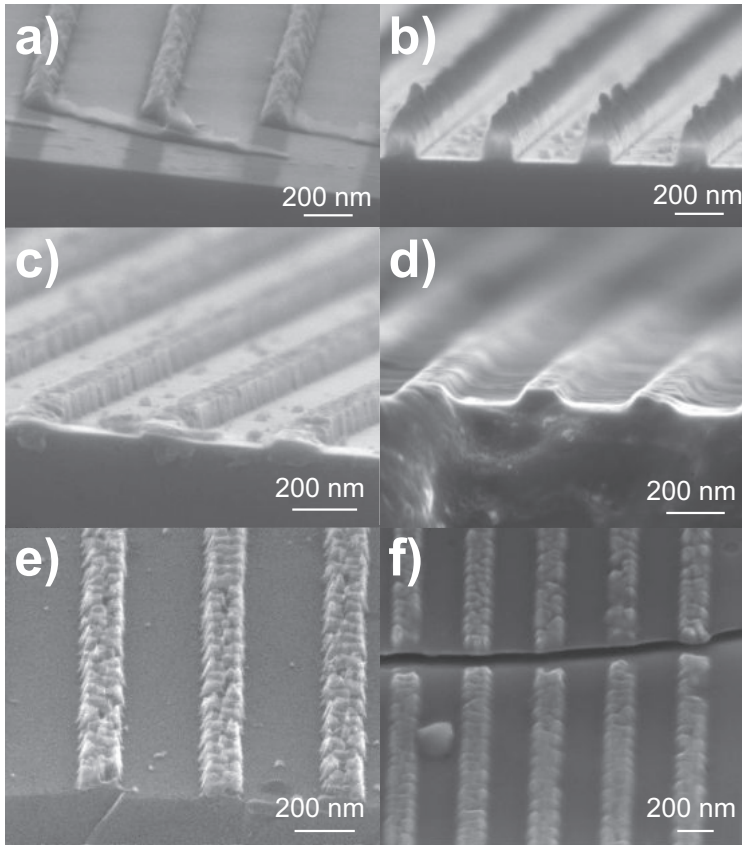


Figure 5.12: SEM images of the patterned substrate made by NIL: a) Substrate after the mold was removed from the resist (Figure 5.1(c)), b) residual resist was removed by oxygen plasma and the steps were etched into the silicon (Figure 5.1(e)), c) the resist was removed from the silicon by oxygen plasma (Figure 5.1(h)), d) substrate was coated with a thin PGMA layer.

5.3.5 Grafting of polymer brushes into pores of silicon photonic crystals

2D photonic crystal samples on silicon wafer

Hereafter 2D silicon photonic crystals [205] samples were studied to better understand the conditions which are needed to coat the silicon-air interfaces of the pores with polymer brushes. For the samples in this section the polymerization procedure was applied on carefully cleaned substrates. It was not possible to further characterize the quality of the samples after each individual step of the polymerization procedure due to limited time of our project ². Since the standard

²The cleaning procedure described in this chapter was developed under time pressure of allocated beam time in the ESRF synchrotron.

cleaning procedure for silicon and the silane monolayer surface functionalization of the activated silicon are well developed and confirmed in the previous Chapters 2 and 3, the focus of the research in this chapter was on the PGMA-coated substrates. The substrates were imaged by high-resolution SEM with the aim to visualize the presence of a polymer brush film inside the pores. Figure 5.13(a) shows the clean silicon sample 2DPC after the furnace treatment. Figure 5.13(b) shows a cleaved substrate which underwent ATRP of glycidyl methacrylate.

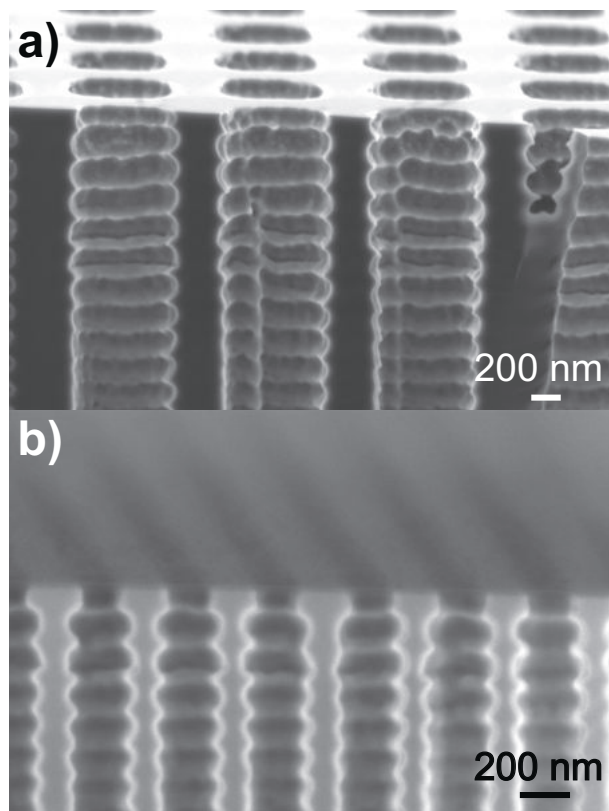


Figure 5.13: SEM images of the 2D silicon EasyCleave sample 2DPC: a) the sample is shown after the furnace treatment, before the polymerization procedure step, b) after using the polymerization procedure step to graft PGMA brushes from the clean silicon surface. Even for smaller pores, as chosen here, the pore openings are not blocked by the polymer layer. The loss of resolution is a potential indicator of an insulating layer added to the sample.

The pores appeared to be coated with PGMA, as indicated by a white layer inside the pores. Table 5.3 shows the EDX measurements before and after the polymerization step. The atom percentages for carbon and oxygen had increased after the polymerization step. The SEM and EDX results were sufficiently strong positive indications of polymer deposition to go on to the next step, namely to

apply the functionalization to 3D photonic crystals.

3D photonic crystal on silicon bar

In the end, the 3D silicon photonic crystal samples were functionalized by means of silane monolayer functionalization and atom-transfer radical polymerization of PGMA polymer brushes, thus preparing the samples for and covalent attachment of near-infrared emitting lead sulfide quantum dots. Sample 3DPC with 2D and 3D silicon photonic crystals made by DRIE (see materials and methods section for details) was cleaned with the procedure described in the previous section. The freshly cleaned silicon bar was activated with piranha solution before the chemical vapor deposition of (3-(2-bromoisobutyryl)propyl)dimethyl-chlorosilane (ATRP initiator). The droplet spread on the silicon surface and the contact angle was $22.6^\circ \pm 2.9^\circ$. For comparison a typical contact angle for a flat substrate after piranha solution would be around 10° . The contact angles confirmed the hydrophilic nature of the surface which meant firstly that the silicon bar was clean and secondly suggested the presence of silanol (Si-OH) groups on the surface. These silanol groups were crucial since the ATRP initiator only covalently binds to the substrate if the silicon-to-oxygen bond can be formed. The activated silicon surface was then reacted with the silane compound to form a monolayer. The successful formation of a monolayer was verified by contact angle measurements. The contact angle was $86.5^\circ \pm 1.3^\circ$. In case of a monolayer present on a flat sample the resulting contact angle would have increased to close to 90° . The surface was expected to be highly hydrophobic due to the bromoalkyl moiety of the initiator, exposed to the outside of the sample.

In the next fabrication step the polymer brushes were grafted from the substrates. Since the polymerization procedure led to thin polymer layers with an aimed thickness of around 40 nm, the resulting effect on the contact angle was assumed to be small but noticeable. A lower contact angle compared to the monolayer was observed, namely $66.2^\circ \pm 1.3^\circ$. This result can be explained by the more hydrophilic nature of the PGMA layer on the silicon-air interface of the bar. A more detailed analysis of the samples was performed with X-ray fluorescence tomography, as is described in Chapter 6. At this stage it was concluded that the silicon surface of the bar was successfully coated with a thin polymer film.

5.4 Summary and outlook

In this chapter we have presented an extensive cleaning procedure that can be applied to flat and 2D and 3D porous samples so that polymer brush layers can be attached to their surface. A combination of chromium etching, RCA-2 cleaning, nitric acid rinsing, and ashing of the fluorocarbons at 800°C in a furnace has provided clean silicon surfaces. The samples were inspected with SEM, EDX and contact angle measurements to check the quality of the individual cleaning steps. The work described in this chapter has provided the crucial step before functionalization of 3D photonic crystals with polymer brush layers and quantum dots.

The polymer used in this chapter offers by the presence of reactive side chains the opportunity to attach molecules and nanoparticles by nucleophilic substitution. This method can be directly applied to bind appropriately functionalized quantum dots. The detailed analysis by X-ray fluorescence tomography after the final fabrication step by infiltrating lead sulfide quantum dots into the pores of the silicon photonic crystals is presented in Chapter 6.

CHAPTER 6

Targeted positioning of lead sulfide quantum dots in 3D photonic band gap crystals revealed by synchrotron X-ray fluorescence tomography

It is a major outstanding goal in nanotechnology to precisely position functional nanoparticles, such as quantum dots, inside a three-dimensional (3D) nanostructure in order to realize innovative functions. Once the 3D positioning is performed, the challenge arises how to non-destructively verify where the nanoparticles reside in the 3D nanostructure. Here, we study 3D photonic band gap crystals made of Si that are infiltrated with PbS nanocrystal quantum dots. The nanocrystals are covalently bonded to polymer brush layers that are grafted to the Si-air interfaces inside the 3D nanostructure using surface-initiated atom transfer radical polymerization (SI-ATRP). The functionalized 3D nanostructures are probed by synchrotron X-ray fluorescence (SXRF) tomography that is performed at 17 keV photon energy to obtain large penetration depths and efficient excitation of the elements of interest. Spatial projection maps were obtained followed by tomographic reconstruction to obtain the 3D atom density distribution with 50 nm voxel size for all chemical elements probed: Cl, Cr, Cu, Ga, Br, Pb. The quantum dots are found to be positioned inside the 3D nanostructure, and their positions correlate with the positions of elements characteristic of the polymer brush layer and the ATRP initiator. We conclude that X-ray fluorescence tomography is very well suited to non-destructively characterize 3D nanomaterials with photonic and other functionalities.

6.1 Introduction

In this representative study, we fabricate three-dimensional (3D) photonic band gap crystals from silicon with the diamond-like inverse woodpile structure consisting of two perpendicular arrays of interpenetrating nanopores [213], see figure 6.1(a). We infiltrate functional quantum dot nanoparticles in these crystals

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that are precisely positioned relative to the silicon-air interfaces by means of polymer brushes [123, 200] that grow from initiator molecules placed on the internal silicon interfaces, see figure 6.1(b). In previous photonic band gap crystal studies, quantum dots were randomly positioned in the crystal [35], whereas brushes will allow to selectively position the dots at places where they experience the maximal band gap effects [53]. Here we employ a polymer brush layer with thicknesses in the 10s nm range (see Chapter 3) to control the distance of an emitter to the pore wall of a 3D crystal. The emission properties of an emitter vary spatially on the 100s nm scale [20]. Therefore there is the need to position the emitter with a precision better than $\Delta x < 100$ nm to control the optical properties of the emitter. Once a 3D nanophotonic structure is functionalized by means of surface chemistry, the characterization method should be *non-destructive* to allow further experimental testing. Therefore it should offer a high resolution in the 10s nanometer range within the range of LDOS variations, and be element specific. Therefore, the first requirement is to find a probing method that provides local information deep inside a 3D nanostructure with nanometer spatial resolution. A second requirement is that the method is element specific to verify that the infiltrated nanocrystals are located in the desired positions and to characterize the infiltration mechanism or process. A third major requirement is that the probing technique must be non-destructive, hence the nanomaterial remains functional and ready for further integration after the inspection. While the widely used scanning electron microscopy (SEM) non-destructively reveals the periodically ordered external surfaces of the photonic crystal (Figure 6.1(c)), internal nanoparticles are hidden, even at a much higher resolution. A common approach in nanotechnology to view elements inside 3D nanostructures is to cleave or ion-mill the sample and then probe the exposed surface with energy dispersive X-ray spectroscopy [214], time-of-flight secondary-ion mass spectrometry [215], X-ray photoelectron spectroscopy [216], or Fourier-transform infrared or Raman spectroscopy [217]. A major disadvantage of this approach is that it is *destructive*. Moreover, several of the probing methods have coarse spatial resolutions in the range of 10 μm or even coarser. X-ray techniques offer suitable non-destructive analysis methods due to their high penetration and high resolution [218, 219]. Anomalous small-angle scattering of X-rays allows to obtain contrast variation in a multicomponent system [220, 221]. Unfortunately, the number of elements that can be distinguished is limited because many incident X-ray wavelengths have to be independently tuned, and it is very difficult to obtain local information from such a scattering method. Here, we demonstrate the use of X-ray fluorescence tomography using a synchrotron source [222–224], that meets all above requirements, to inspect designed functional nanostructured samples.

6.2 Materials and methods

6.2.1 3D Si photonic crystals

Our 3D photonic band gap crystals were fabricated by a CMOS-compatible fabrication process that is described in detail in Refs. [201, 204, 207]. As substrates, we employ Si beams (cross sections $0.5 \times 0.5 \text{ mm}^2$) that are chemically etched to obtain perpendicular crystal surfaces. A thin 50 nm Cr layer serves as a hard etch mask that is deposited on two adjacent surfaces of a beam. In the Cr layer, we define an etch mask in a single step on *both* faces of the beam using focused-ion beam writing with Ga ions [207]. We perform deep reactive ion etching using the Bosch process (a time-multiplexed alternating process that alternates etching and lamination steps) to etch two perpendicular arrays of deep nanopores [204]. In the etching step, pores are etched with SF_6 and in the lamination step the pore walls are protected with a CF polymer layer. The radius of the nanopores etched in the silicon was designed to be $R = 160 \text{ nm}$, and the lattice parameters are $a = 680 \text{ nm}$ and $c = 481 \text{ nm}$. Figure 6.1 shows a SEM image of a successfully etched photonic crystal. The overlap region of the pores entering into the XY surface (top) and into the XZ surface (bottom) mutually cross inside the beam and form the 3D cubic inverse woodpile structure that has a broad photonic band gap [213, 225]. The size and shape of the resulting 3D cubic inverse woodpile structure depends on the etch depths of the both sets of pores. The deeper each set of pores is etched into the silicon, the larger the volume of the inverse woodpile structure. For this specific sample studied here, the resulting 3D volume was smaller than aimed for. The reason is that the second etching step resulted in shorter pores than the first one etched due to high amounts of fluorocarbons on the surface for the second set of pores. Therefore, the pores in the X-direction do not cross all pores etched in the Z-direction (see Fig. 6.1(a)), therefore, at larger X-positions there is a 2D crystal of Z-directed pores adjacent to the 3D crystal structure near the edge of the wafer.

In Table A.1 of the Appendix we present an overview of the studied samples. In total three 3D silicon photonic crystals were studied by X-ray fluorescence tomography. For all these 3D silicon photonic crystals 3DPC1, 3DPC2 and 3DPC3 we collected complete X-ray datasets. In this chapter we only show results for the completely analyzed dataset of structure 3DPC1. For the fitted dataset on 3DPC2, an insufficient amount of the 24 angles could be corrected, unfortunately not enough for tomography reconstruction. The dataset for 3DPC3 was fitted to obtain the areal mass density which we converted into areal and volume atomic densities for each species. The volume reconstruction is still to be done.

6.2.2 Synchrotron X-ray fluorescence (SXRF) tomography

Figure 6.2 shows the setup to perform X-ray fluorescence nano-tomography at ESRF beamline ID16A [226, 227]. X-ray fluorescence is excited by the incident beam (FWHM widths $\Delta X = 23 \text{ nm}$ and $\Delta Y = 37 \text{ nm}$) with a photon energy set to 17 keV with a 1% relative bandwidth. The X-ray beam is focused by multilayer coated Kirkpatrick-Baez (KB) optics onto the sample. At every sam-

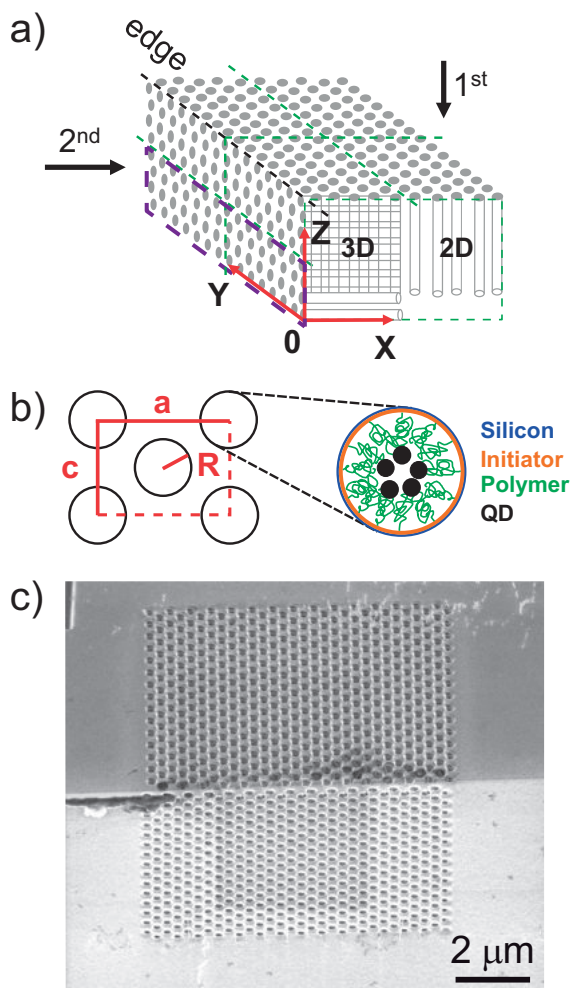


Figure 6.1: 3D photonic crystal and chemical positioning of quantum dots inside of the nanostructure. (a) Schematic of an inverse woodpile photonic crystal on the edge of a silicon beam. Green dashed lines indicate the two surfaces into which nanopores are etched. The 3D and 2D parts of the crystal are indicated in the XZ front face. (b) View along the pores showing the lattice parameters a, c (with $a = \sqrt{2}c$) and pore radius R . Zoomed-in cross section of one pore with targeted surface-chemistry: ATRP initiator layer (orange), polymer chains forming brushes (green) and covalently attached PbS quantum dots (black) on top of silicon (blue). (c) Scanning electron microscope (SEM) image of a 3D photonic crystal viewed from 45° on the edge of the silicon beam showing the XY (top) and the XZ surfaces (bottom); the scale bar indicates 2 μm.

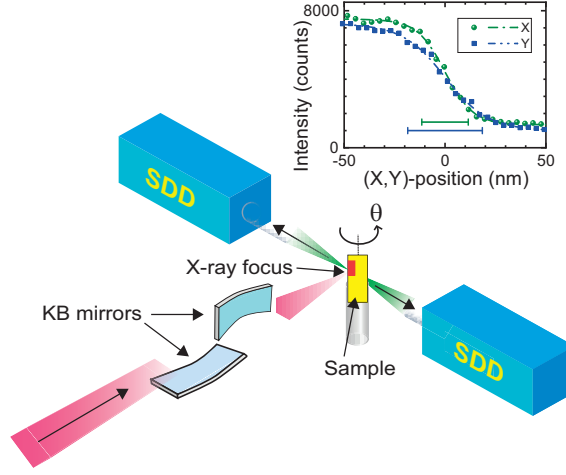


Figure 6.2: Schematic of the X-ray fluorescence setup. The X-ray beam arrives from bottom left, is focused by Kirkpatrick-Baez (KB) optics on the sample. The fluorescent light is detected by two silicon drift detectors (SDD) placed at $\pm 90^\circ$ with respect to the incident beam. The sample is rotated angle θ about the vertical axis. The inset presents the knife edge measurements of the excitation beam (intensity versus X- or Y-position) for a calibration sample. The resulting full widths at half maximum (FWHM) are $\Delta X = 23$ nm and $\Delta Y = 37$ nm.

ple orientation θ , the exciting X-ray focus is continuously scanned through the crystal in the horizontal direction and step-wise in the vertical direction to image the whole crystal. This corresponds to maps with 240×240 pixels (50 nm size), corresponding to a total area of $12 \times 12 \mu\text{m}^2$. At each sample position (x_i, y_j) the X-ray fluorescence photons are collected by two six-element silicon drift diode detectors with an energy resolution of 130 eV at 5 keV photon energy that are placed at $\pm 90^\circ$ with respect to the incident beam; their readings are combined into an energy-resolved spectrum $I(E, \theta, x_i, y_j)$. For further background including introductory material, see Section A.1 in the Appendix.

The chemical species that can be detected depends on the constituent elements and their fluorescence spectra. Whether such an element can be detected depends on whether its transition fits in the available spectral range, as shown in Fig. 6.4. The available range in turn depends on factors like the excitation energy (here 17 keV) and a possibly present substrate or matrix (here the silicon backbone of the photonic band gap crystal) that emits intense peaks (here at 1.74 keV).

We note that there are fundamental limitations to the detection based on the involved chemical species and on their combination. On one hand, heavy elements are more readily detected since the photon energy of their fluorescence is sufficiently high to be detected, see Fig. 6.4. In our case, Pb peaks are strong and clearly detected at 10.5 keV and 12.5 keV, whereas the Cl peak (2.6 keV) at a low photon energy is swamped by S and Pb transitions. On the other hand,

if combinations of elements yield overlapping fluorescence peaks, this also affects their detection, *e.g.*, in our case the S K_{α} peak (near 2.3 keV) cannot be properly modeled since it overlaps with the Pb M_{α} transition. Each detection pixel has an area of $50 \times 50 \text{ nm}^2$. The integration time at each sample position was set to 50 ms. The flux of 7.5×10^9 photons/s is kept far below the maximum flux to prevent detector saturation, hence collecting one 240×240 pixel fluorescence image took about 1 hour, and collecting a full tomographic scan over 17 angles took about 20 hours, excluding the time for alignment. In view of the current measurement time and data analysis, the SXRF method is not yet suited to iteratively optimize the infiltration.

The sensitivity of the method is estimated to be 0.4 ppm for the relative density of Pb atoms (of the quantum dots) versus Si atoms (of the photonic crystal backbone.) We obtain this sensitivity by firstly calculating the total number of lead atoms for the entire crystal volume from our data (integrating Fig. 6.7(e)), secondly from that value we estimate the density of lead atoms per cubic micron, thirdly, we compare that value with our estimation of the silicon atoms per micron. Hence we detect 24000 Pb atoms compared to 50×10^9 Si atoms = $24000 / 50 \times 10^9 = 0.4 \text{ ppm}$.

Volume reconstruction

In the volume reconstruction the mass density distribution is reconstructed from the angular projections through tomographic reconstruction. In this case the Radon transform is severely undersampled and iterative, algebraic reconstruction methods have to be used. The volume reconstruction consists essentially of three steps: A) a drift correction on the projections, B) the tomographic reconstruction, C) corrections for self-absorption.

A) *Drift correction*: Due to the very long measurement times, lateral drifts occur that have to be corrected. The alignment was carried out with ESRF in-house software using the GNU Octave (<http://www.octave.org>) programming environment and the TomoJ plugin of the public domain image analysis program ImageJ (<http://rsbweb.nih.gov/ij>). The vertical and the horizontal drifts were separately corrected using the preservation of the vertical mass profile under rotation [228] and the landmarks refinement of the TomoJ plugin, respectively. Gallium, the element that exactly defines the position of the pores, was used as the reference element for the drift correction. During the writing of the etch mask by focused-ion beam (FIB) the chromium hard mask is bombarded with gallium ions. That means that gallium is present on the surface at the locations where the pores are written. We used 4 landmarks on the elbow-shaped marker as suitable reference points. The data were corrected in such a way that the location of a specific landmark describes a sinusoidal trajectory for the different rotation angles. The drifts, as determined for gallium, were then compensated for on all elements using bicubic interpolation.

B) *Volume reconstruction*: Since the number of successfully collected projections was only 17, a regularized iterative tomographic reconstruction method was chosen. We used the Total Variation Minimization (TVM) method with a positivity constraint as implemented in the PyHST software developed

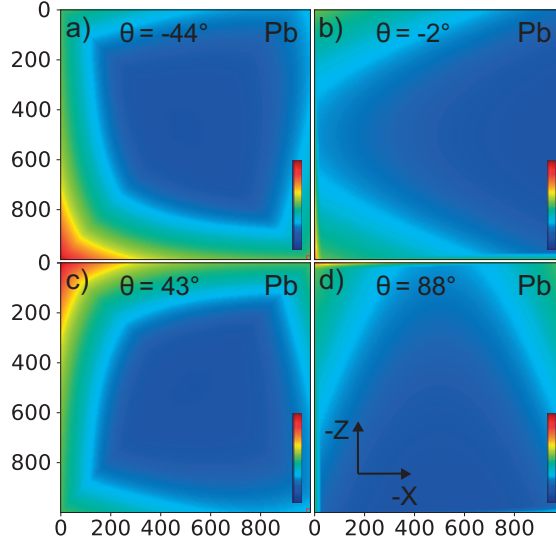


Figure 6.3: Attenuation maps of lead fluorescence as a function of atomic position inside the Si beam. In this representation, the Si-beam orientation is fixed with the photonic crystal (small square) at bottom right, whereas the incident X-ray beam orientation is varied: a) $\theta = -47^\circ$ beam incident from bottom left, b) $\theta = -2^\circ$ beam from left, c) $\theta = 43^\circ$ beam from top left, d) $\theta = 88^\circ$ beam from top. All color bars run from 0 to 1.

at ESRF [229]. The parameters for the regularization and the number of iterations were adjusted visually for the best outcome of the reconstruction. The final conditions of the reconstruction were as follows: 300 iterations of the Chambolle-Pock optimization algorithm without pre-conditioning and with positivity constraint and a TV regularization parameter of 10^{-5} and 10^{-3} , respectively, for the elements Ga and [Br, Pb]. The sample substrate induces that the tomography is local in nature. To compensate for this the projections were padded horizontally by extension with the last value and the support of the volume reconstruction was taken to be a cylinder with 240 pixels height and 300 pixels diameter, *i.e.*, slightly wider than the original projections.

C) *Self absorption*: To estimate the effect of the self absorption, we used the package *PyCorrectedEmissionCT* [230]. Attenuations were included of both the incident 17 keV X-ray beam and of the emitted X-ray fluorescence along its path to the detectors. We modelled the sample by a Si beam with $500 \times 500 \mu\text{m}^2$ cross section and in one corner a $8 \times 8 \mu\text{m}^2$ region with half the density of silicon representing the photonic crystal. For each element under study, a weighted average energy of the X-ray fluorescence was considered, and the corresponding attenuation coefficient was calculated using the Xraylib library [231]. Next, attenuation maps per element were calculated for all angles of the tomography scan. As an illustration, Figure 6.3 shows the result for the Pb fluorescence at four angles, which show that the angle-dependent attenuation is fairly constant.

Therefore, and to keep the tomographic inversion tractable, we chose to compensate for the self absorption by scaling-up all tomography by the inverse of the mean attenuation, averaged spatially over the photonic crystal and averaged over all tomography angles. This mean attenuation amounts to 0.168, 0.404, 0.415, 0.445 and 0.439, respectively for Cl, Cu, Ga, Br and Pb.

6.3 Results and Discussion

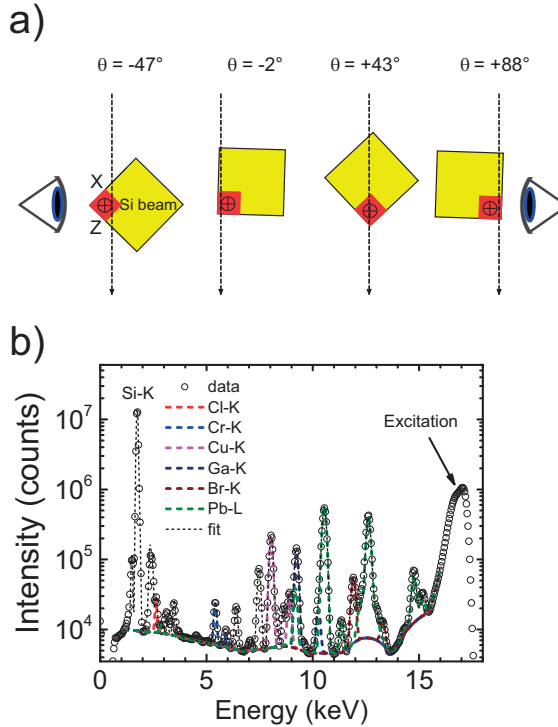


Figure 6.4: Sample mounting and X-ray fluorescence spectra. (a) Top view showing how the X-ray beam traverses the sample on the Si substrate at four different angles θ . Two detectors collect X-ray fluorescence signal on the left and right sides. (b) X-ray fluorescence spectrum $I(E, \theta)$ (circles) of one of the crystals averaged over all 240×240 pixels in the image at $\theta = -47^\circ$. The analyzed Cl, Cr, Cu, Ga, Br, Pb transitions are shown in order of increasing photon energy.

In X-ray fluorescence tomography, the sample is illuminated with a finely focused X-ray beam to excite X-ray fluorescence that is characteristic for each element in the sample, see figure 6.4(a). At $\theta = -47^\circ$ the incident beam passes obliquely through the crystal. The right detector will detect the fluorescence signal that is integrated along the incident X-ray beam (the left detector will detect little signal as it is attenuated by the substrate.) At $\theta = -2^\circ$ the incident beam traverses the whole $500 \mu\text{m}$ -thick Si substrate, which is feasible on account of

the high photon energy of 17 keV. The detected fluorescence signal is integrated along the X-direction, hence the left detector effectively sees a projection of the object in the YZ-plane. At $\theta = 43^\circ$ the incident beam first passes through even more substrate thickness (by projection) before entering the photonic crystal. Both detectors see an oblique projection of the sample. At $\theta = 88^\circ$ the X-ray beam travels nearly in the high-symmetry $-Z$ -direction, the (left) detector detects fluorescence integrated along the $-Z$ -direction and thus effectively detects a projection of the object in the XY-plane.

Figure 6.4(b) shows a typical X-ray fluorescence spectrum that is averaged over all 240×240 pixels. We identify the involved elements from their known X-ray emission with constraints from the known chemical compounds involved in the sample preparation (see Chapters 3 & 5). The peak at 1.74 keV is the Si- K_α transition from the photonic crystal matrix. In order of increasing photon energy, chlorine, chromium, copper, gallium, bromine, and lead are detected. Chlorine features in the Cu(I)Cl species used as catalyst in the polymerization and in the termination group of the polymer brushes (see figure 6.1(b)). Chromium appears in the sample as the hard-mask material for the deep reactive-ion etching of the pores that define the 3D photonic crystal. Copper is introduced by the two catalyst species Cu(I)Cl and Cu(II)Br₂ that are incompletely washed out due to the limited permeability of such a complex 3D porous nanostructure. Gallium occurs since it is used to write the etch mask by means of focused-ion beam milling. Bromine features in the ATRP-initiator monolayer for the brush synthesis and also in the Cu(II)Br₂ catalyst species used in the polymerization (see figure 6.1(b)). Finally, lead is the signature of the infiltrated PbS quantum dots with a strong signal since it is a heavy element. We note that sulfur from the quantum dots is not detected, since the signal is attenuated due to the low photon energy and is likely overwhelmed by the strong Si K_α peak at 1.74 keV. The peak at 17 keV is the excitation by the incident X-ray beam that is broadened due to Compton scattering and a finite detector resolution.

At every sample orientation θ (figure 6.4(a)), the X-ray focus is raster scanned through the crystal. The X-ray fluorescence signals separated for all elements yield so-called projection maps. These are 2D maps of the elemental number density per pixel area integrated along the X-ray beam while it traverses the sample. Figure 6.5 shows examples for Ga and Br at two different orientations θ that we will discuss.

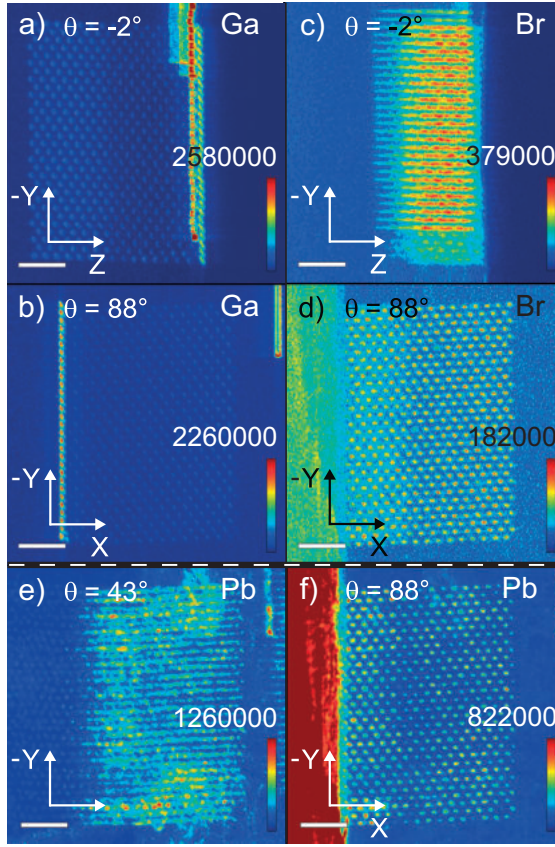


Figure 6.5: Projection maps of the number of Ga, Br and Pb atoms per pixel (with area $50 \times 50 \text{ nm}^2$), integrated along the propagation direction of the beam, for sample orientations: a) Ga at $\theta = -2^\circ$, b) Ga at $\theta = 88^\circ$, c) Br at $\theta = -2^\circ$, d) Br at $\theta = 88^\circ$, e) Pb at $\theta = 43^\circ$, e) Pb at $\theta = 88^\circ$. Color bars with the density scales are given in each panel.

Figure 6.5(a) shows the gallium signal projected on the YZ plane. From left to right, we see (faintly) the nanopore entrances (on the YZ crystal surface) that are defined in the lithography step by focused-ion beam milling using Ga ions. At two thirds from the left, there is a bright streak of Ga-signal in the Y-direction, because the fluorescence signal is added (projected) in the X-direction for all nanopore entrances in the XY crystal surface.

Figure 6.5(b) shows the gallium signal projected on the XY plane. At one fourth from the left, there is a bright streak of Ga-signal in the Y-direction, because the fluorescence signal is added (projected) in the Z-direction for all nanopore entrances in the YZ crystal surface. Further to the right, we (faintly) see the nanopore entrances on the XY crystal surface. These observations reveal that the gallium atoms are effective markers of the external crystal surface.

In Figure 6.5(c) we observe the Br density in the photonic crystal from a high-

symmetry angle viewing along the X-axis onto the YZ plane. The Br density is arranged in horizontal stripes, due to the Z-directed pores. Therefore, we conclude that Br is present throughout the whole extent of the nanopores. Thus, the ATRP-initiator has infiltrated the pores of the 3D silicon photonic crystal to form a monolayer throughout the whole structure (based on previous results on flat Si wafers [123]), which is crucial for further functionalization of the surface inside the 3D silicon crystal pores. It is also conceivable that part of the Br density is caused by incompletely rinsed Cu(II)Br₂ catalyst that is used in the synthesis. In both cases, we conclude that intended chemistry has taken place inside the nanopores.

In Figure 6.5(d) we observe the projection in the XY plane that shows the periodicity of the nanopores as individual disks of Br atoms. We do not observe thin circular shapes as expected in case of purely surface deposition on perfectly cylindrical pores. Since the pores are not perfectly perpendicular to the XY-plane and have a depth-dependent diameter (known as tapering [204]), the projected Br density appears as filled ellipses.

On the left side the edge of the silicon beam is visible. Figure 6.5(e) shows the lead signal projected at $\theta = 43^\circ$, which shows a diagonal projection of the crystal (compare Fig. 6.4(a)). The projection shows that the Pb atoms (and thus the quantum dots) form horizontal stripes, just the nanopores at such a projection. Therefore, this is a first indication that the Pb atoms have infiltrated in the 3D nanostructure.

In Figure 6.5(f) we observe the projection in the XY plane that shows the periodicity of the nanopores as disks of Pb atoms. The high density on the left side of the image is caused by the incident beam being nearly parallel to the sample surface (compare Fig. 6.4(a)) and thereby exciting many Pb atoms on the whole external surface of the Si sample.

Projection maps are collected while rotating the sample by 180° , see figure 6.4(a). After tomographic reconstruction (see Section 6.2.2), one obtains a position-resolved 3D density map of all elements that are detected inside the nanostructure. In case of Cl and Cr, the signals were relatively weak (only a few times 10^4 counts after background subtraction) so that their projection maps were relatively noisy, hence no firm conclusions could be drawn on the positions of these elements.

Figure 6.6(a,b) show XZ cross sections of the 3D density map of gallium $N_{v,Ga}$ (X, Y, Z) (the whole data set is shown as a Y-scan of X-Z cross sections in Supporting Information Movie S1 in Ref. [161]). The gallium is located near the external surfaces of the photonic crystal, which is reasonable since Ga-ions are used to define the etch masks for the nanopores on the external surfaces of the Si beam substrate by focused-ion beam milling [207]. Since there is hardly any Ga-signal from the bulk of the Si substrate, there are few artifacts due to the tomographic image reconstruction, which confirms that the reconstruction has converged well.

Figures 6.6(c,d) show XZ cross sections of the 3D density map of bromine atoms $N_{v,Br}$ (X, Y, Z), see Figure 6.1(b). The Br density is distributed in vertical stripes in the Z-direction, showing that the Br atoms have infiltrated the nanopores, to

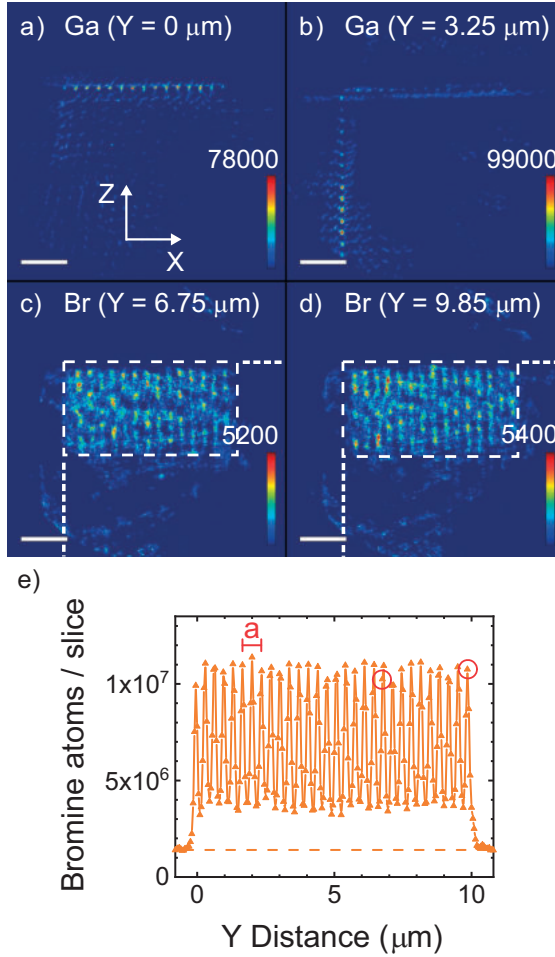


Figure 6.6: XZ cross sections of the Ga atomic density at depths $Y = 0 \mu\text{m}$ (a) and $Y = 3.25 \mu\text{m}$ (b). XZ cross sections of the Br atomic density at $Y = 6.75 \mu\text{m}$ (c) and $Y = 9.85 \mu\text{m}$ (d). The scale bars represent $2 \mu\text{m}$, the intensity bars the number of atoms per voxel (with volume 50^3 nm^3) and white dashed lines delineate the crystal's cross section and the external surface. (e) Number of bromine atoms per slice integrated along Z , as a function of Y . The lattice parameter a of the photonic crystal is shown. The periodicity of the pores is clearly visible. Red circles indicate the Y -coordinates in c) and d).

as deep as $\Delta Z = 3.5 \mu\text{m}$. All Z -directed nanopores are filled from the sample surface, since all pores over an X -extent $\Delta X = 7.2 \mu\text{m}$ reveal similar Br density profiles. We also observe that Br-atoms are infiltrated in the X -directed pores at intermediate Y -coordinates (see Supporting Information Movie S2 in Ref. [161]). Thus, the Br atoms effectively outline the nanopore structure in the silicon. These observations match our expectations because the initiator molecules were

introduced as a vapor that readily diffuses into a porous sample. Therefore, the silane monolayer due to the ATRP deposition method resides on the surfaces of the nanopores. The presence and homogeneity of the silane monolayer influences and defines the subsequent functionalization with the polymer brush layer.

Figure 6.6(e) shows the total number of Br atoms per XZ slice as a function of Y-position. We observe that the bromine density shows a sine-like profile in the whole crystal between $Y = 0$ to $10\ \mu\text{m}$. The period is equal to $(a/2)$ which is sensible because fluorescent signal from inside the pores is observed *twice* per unit cell since there are two planes of pores within each unit cell, as shown in Figure 6.1(b). We observe that the maximum amplitude is constant to within 13% and the minimum amplitude is constant to within 21%, confirming a fairly homogeneous infiltration. The open red circles mark the Y-positions of the slices in Figures 6.6(c,d). We therefore conclude that the upper amplitude represents the bromine densities in the pores in Z-direction, whereas the lower amplitude represents the bromine densities in the pores in the X-direction. The amplitude oscillates between 3.6×10^6 and 0.8×10^7 bromine atoms per slice, whereas the finite density outside the crystal is 1.3×10^6 bromine atoms per slice. When we correct the densities in the crystal for this background, the density in the pores in the Z-direction equals $(9.4 \times 10^6 / 2.2 \times 10^6) = 4.3\times$ greater than in the pores in the X-direction. One possible explanation for the different average Br densities is that the pores in the X-direction were etched in the second etching step with the presence of fluorocarbons on the YZ surface. It is then conceivable that these fluorocarbons that were used in the protection steps of the etching process were incompletely removed by the oxygen plasma cleaning in the etching machine after the etching of the first set of pores in the Z-direction, thereby (partly) blocking the infiltration of these nanopores. Figure 6.7(a,b) show XZ cross sections of the 3D density map of lead atoms $N_{v,Pb}$ (X, Y, Z), which are the cations of the infiltrated PbS quantum dot nanoparticles, see figure 6.1(b). The Pb density extends along the pores in the Z-direction, starting from the XY top surface and extending about $3.5\ \mu\text{m}$ into the crystal.

Figure 6.7(c) show a YZ cross section of the 3D density map of lead atoms $N_{v,Pb}$ (X, Y, Z). The quantum dots extend along the pores in the Z-direction, starting from the XY top surface and extending about $3.5\ \mu\text{m}$ into the crystal (the whole data set is shown as a Y-scan of X-Z cross sections in Supporting Information movie S3 in Ref. [161]).

Figure 6.7(d) show a YX cross section of the 3D density map of lead atoms $N_{v,Pb}$ (X, Y, Z). The pores are visible as small dots on the XY surface. We conclude that the quantum dots have indeed been successfully infiltrated into the nanopores of the 3D photonic crystal.

To characterize in more detail the infiltration of the quantum dots in each nanopore, we plot in figure 6.7(e) the density of lead atoms integrated along Z as a function of Y-coordinate. The Pb density oscillates throughout the whole crystal between $Y = 0$ to $10\ \mu\text{m}$ with a period equal to $(a/2)$, as with the Br data in figure 6.6(e), due to two planes of nanopores per unit cell. The Pb density amplitude in Figure 6.7(e) oscillates between 1.8×10^7 and 6.8×10^7 lead atoms per slice. Outside the crystal, the lead density is between 1.8×10^7 and 2.1×10^7

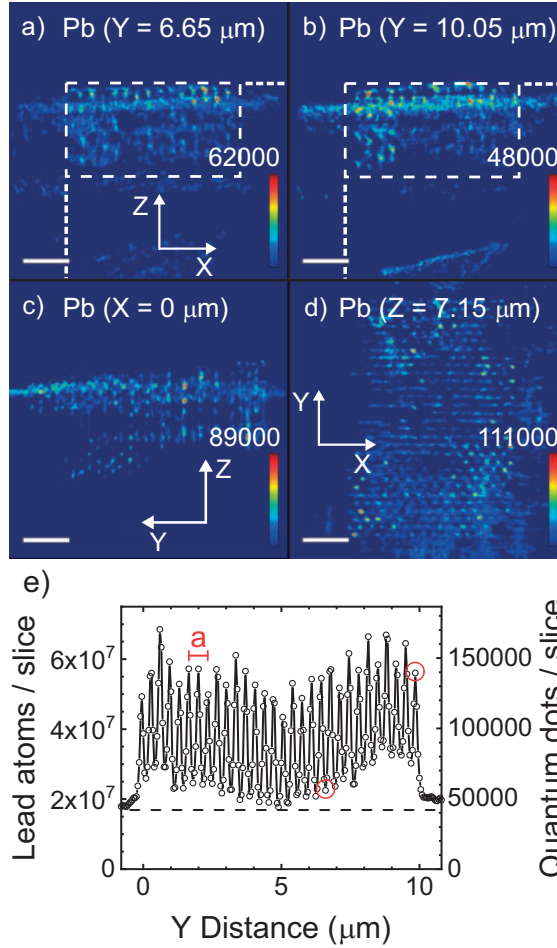


Figure 6.7: (a, b): XZ cross sections of the reconstructed sample volume for the Pb atoms at depths $Y = 6.65 \mu\text{m}$ (a), $Y = 10.05 \mu\text{m}$ (b). The scale bar represents $2 \mu\text{m}$, the intensity bar the number of lead atoms per voxel and white dashed lines delineate the crystal's cross section. (c): YZ cross section of the reconstructed sample volume for the Pb atoms at depths $X = 0 \mu\text{m}$. (d): XY cross section of the reconstructed sample volume for the Pb atoms at depths $Z = 7.15 \mu\text{m}$. (e) Density of lead atoms per XZ-slice *versus* Y , the right ordinate shows the corresponding number of quantum dots (taking 465 Pb atoms per dot). The lattice parameter a of our photonic crystal is indicated. The periodicity of the pores is clearly visible. The red circles show the Y -coordinates in (a) and (b).

atoms/ $(50 \text{ nm} \times 50 \text{ nm} \times 3.5 \mu\text{m})$ which is mostly determined by quantum dots on the external sample surface (a real signal) and by artifacts due to the 2D structure that lies behind the 3D structure. At $Y = 5 \mu\text{m}$ the Pb density modulation is somewhat reduced before increasing again towards the right edge of the crystal at $Y = 10 \mu\text{m}$.

Since we know from the Br density (see figure 6.6(c,d)) that the Z-directed nanopores have a depth of 3.5 μm , the exhilarating conclusion arises that the quantum dots have been successfully infiltrated over the full depth of the nanopores. Similar to Br at other Y-coordinates (see Supporting Information Movie S2 in Ref. [161]), we also observe Pb over the full depth of the X-directed pores. Therefore, our strategy to infiltrate quantum dots inside 3D nanostructures by attaching them to polymer brushes has been successful. Moreover, this result demonstrates that X-ray fluorescence tomography is a powerful method to characterize the infiltration of functional nanoparticles in complex 3D architectures.

We observe that the maximum amplitude in Figure 6.7(e) is constant to within 37% and the minimum amplitude is constant within 50%. These amplitudes for the lead atoms are less homogeneous than for bromine, which is reasonable for three reasons. (i) The Br atoms originating from the initiator molecules are introduced in the vapor phase, hence the diffusion is the fastest, leading to the most homogeneous infiltration. Moreover, the rinsing of excess molecules of this species also likely has the most homogeneous distribution. (ii) The bromine atoms originating from the Cu(II)Br_2 catalyst occur in the polymerization solution. These bromine atoms diffuse less readily in the nanopores than the bromine atoms (in the initiator) introduced *via* the vapor. (iii) Since the quantum dots that are introduced as nanoparticles in suspension are much larger than the initiator and the catalyst compounds, it is a reasonable inference that the QDs diffuse even less readily than the vapor and the polymerization solution, thereby leading to a greater inhomogeneity. Moreover, additional inhomogeneity arises during the rinsing of excess of quantum dots after infiltration. Based on the details explained above, we expect that the maximum and the minimum amplitudes of the lead signal vary more than for bromine.

Let us evaluate our results in light of the three main requirements that we set out with. Firstly, we aimed for (a) nanometer resolution (b) at great depths inside 3D nanostructures. (a) At present, the resolution is determined by the size of the X-ray focus (23 nm by 37 nm, see inset of Figure 6.2) and the step size of the spatial scan (50 nm), where the latter was in turn set by the total measurement duration. It would be advantageous to further improve the resolution as it would allow to resolve the brush thickness. A straightforward way to improve the resolution such that it is limited only by the focus size, is to increase the incident photon flux and improve the detector technology. This is exactly what is being done in the ongoing refurbishments of several large synchrotrons including ESRF. The increased coherence of the new synchrotron X-ray beams will also allow for employing smaller foci and hence a further improved resolution. (b) To probe elements deep inside nanostructures, we employed high-energy X-ray photons (17 keV) to achieve a high penetration depth. Such a high photon energy also allows for samples to be integrated on thick substrates like wafers [232]. At the ID16A instrument used in the present study, it is also feasible to excite at an even higher photon energy of 33.5 keV, but this makes little sense since a major limitation is the absorption of the emitted X-ray fluorescence that has a fixed energy. Exciting at higher photon energy will reduce the excitation efficiency and therefore also reduce the sensitivity. Our choice of 17 keV is nearly ideal to excite all elements

up to Br (absorption edge at 13.5 keV) and Pb (highest L-edge at 15.9 keV). The K-edge of Pb at 88 keV is out of reach with nano-focusing, moreover, exciting this absorption edge would result in highly inefficient excitation of other, lighter, elements.

Secondly, we aimed for element specific detection. Indeed, we successfully detected Br, Ga, Pb and Cr with a high signal to noise ratio. For Cl and Cu the collected data had a low signal to noise ratio, due to a surface contamination that was hiding the weaker bulk signal. Moreover, the signal of these low-Z elements at relatively low photon energy is susceptible to self-absorption by the bulky sample. The outcome could potentially be improved for these low-Z elements by using a confocal detection scheme [233] or wavelength dispersive X-ray spectroscopy [234]. Nevertheless, combining these techniques with nano-tomography remains a major technical challenge. It is an interesting suggestion to design the monomer for the polymer synthesis with a heavier element as a marker, such that it is more readily detected by X-ray fluorescence.

Thirdly, we aimed for a non-destructive probing method. Our method meets this requirement as no irreversible mechanical modifications like cleaving or milling are needed. To further confirm the integrity of our samples, we verified that we could still detect near infrared luminescence from the PbS quantum dots after the X-ray experiments.

6.4 Summary and outlook

We have performed X-ray fluorescence tomography to locate the positions of quantum dots that were infiltrated deep inside a 3D nanostructure, a photonic band gap crystal, made from silicon. This demonstration leads to opportunities in a number of applications; In nanophotonics it is known that the fundamental local density of optical states (that controls the fluorescence of embedded emitters) has interesting properties, either maxima and minima, that do not necessarily appear at interfaces between constituent material [5]. For instance, in Ref. [20] it was found that the LDOS has a maximum at low-symmetry positions in the unit cell of inverse opals. Thus, to optimally control an emitter, one has to position the emitter at these positions. Assuming that the technology to position the emitter exists (see, *e.g.*, Ref. [123]), one must then probe the resulting positions to verify the functionality of the device, and this is exactly the step forward offered by the present X-ray fluorescence tomography study. In other technologies, like batteries or sensors, see *e.g.*, Ref. [235], it is vital to position functional nanoparticles on the interfaces between constituent materials or phases, while the functionality or its efficiency greatly decrease if the nanoparticles are displaced. So also for these applications, X-ray fluorescence tomography can verify the intended positions to a high (nanometer) precision, and thereby greatly contribute to improved batteries and sensors.

A positional control of the quantum dots was achieved based on the conclusions of a successful ATRP since the quantum dots would then be located on the polymer layer. It will be shown in Chapter 7 that the positional control of the

quantum dots with a polymer brush layer strongly modifies the emission of the nanocrystals. We have observed up to a 100-fold inhibition of the spontaneous emission.

The next logical step is to increase and vary the polymer layer thickness and keep the structural parameters of the photonic crystal the same. With this approach it will be possible to track if the quantum dot position is controlled by the polymer layer. To further improve the outcome after the volume reconstruction, it would be crucial to measure a complete structure with a resolution of 20 nm or below.

CHAPTER 7

Strongly inhibited spontaneous emission of PbS quantum dots covalently bound to 3D silicon photonic band gap crystals

We present an optical study of the spontaneous emission of lead sulfide (PbS) nanocrystal quantum dots in three-dimensional (3D) photonic band gap crystals made from silicon. The nanocrystals emit in the near-infrared (NIR) range to be compatible with the 3D silicon nanophotonics. The nanocrystals are covalently bound to polymer brush layers that are grafted from the Si-air interfaces inside the nanostructure using surface-initiated atom transfer radical polymerization (SI-ATRP). The presence and position of the quantum dots was previously characterized by synchrotron X-ray fluorescence tomography. We report both continuous wave (cw) emission spectra and time-resolved time-correlated single photon counting. In time-resolved measurements, we observe that the total emission rate greatly increases when the quantum dots are transferred from suspension to the silicon nanostructures, likely due to quenching (or increased non-radiative decay) that is tentatively attributed to the presence of Cu-catalyst during the synthesis. In this regime, continuous wave emission spectra are known to be proportional to the radiative rate and thus to the local density of states. In spectra normalized to those taken on flat silicon outside the crystals, we observe a broad and deep stop band that we attribute to a 3D photonic band gap with a relative bandwidth up to 26%. The shapes of the relative emission spectra match well with the theoretical density of states spectra calculated with the plane wave expansion. The observed inhibition is 4 to 30 times, similar to previously reported record inhibitions, yet for completely coincidental reasons. Our results are relevant to applications in photochemistry, sensing, photovoltaics, and to efficient miniature light sources.

7.1 Introduction

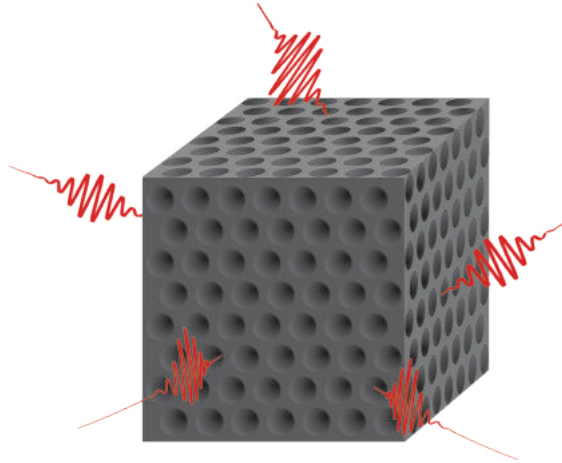


Figure 7.1: Cartoon of a finite three-dimensional (3D) photonic crystal in free space. Since the crystal has a complete 3D photonic band gap, ubiquitous vacuum fluctuations incident on the crystal's surface (shown as red wavelets) are forbidden from entering and are thus reflected from the crystal's surfaces. Hence, an excited two-level quantum system (atom, ion, molecule, or quantum dot) embedded inside the crystal is shielded from the fluctuations and cannot decay by spontaneously emitting a photon. Thus, the excited state becomes more stable.

The intriguing opportunity to control the properties of matter via the properties of light lies at the heart of quantum optics and cavity quantum electrodynamics (cQED). A famous example is the control of the radiative rate of an elementary quantum emitter such as an excited atom, ion, molecule, 2D material, or quantum dot [236]. Such control is essential for applications ranging from miniature lasers and light-emitting diodes [19, 34], to single-photon sources for quantum information [237–239], solar energy harvesting [240, 241], to photocatalysis and photochemistry [242–244], and sensing [245, 246].

When the emitter's properties are in the quantum regime [23], as is the case with nano-emitters in the optical range, a major role is played by the fluctuations of the quantized electromagnetic fields, so-called vacuum fluctuations [247, 248]. Figure 7.1 schematically illustrates such fluctuations, that exist everywhere, even when there are zero photons. By surrounding an emitter by a suitably tailored dielectric nanostructured environment, the vacuum fluctuations are controlled; the most radical control is offered by photonic band gap crystals, as discussed in this chapter. Inside such nanostructures, all light waves (with many photons) and hence all vacuum fluctuations (with zero photons) are forbidden by interference (since both are solutions of Maxwell's equations) and are thus expelled, as illustrated in Figure 7.1.

Long after the pioneering realization by Purcell that an emitter's environment such as a cavity controls the emission rate [249], emission control has become

one of the main drivers of the field of nanophotonics [5, 16, 250–252]. Following seminal work by Bykov and by Yablonovitch [19, 236], emission control was first studied on periodic photonic crystals [35, 45, 159, 180, 253–259], and recently even extended to 3D circuits [260] and chiral emission [261]. Emission control has also successfully been pursued with many different nanophotonic systems and many different quantum emitters, such as atoms and dye molecules in Fabry–Pérot microcavities [262, 263], quantum dots in pillar microcavities [50, 238] and in disordered photonic materials [264], ions in whispering gallery-mode microspheres [265–267], dye molecules in plasmonic nanocavities and on nanoantennae [51, 268–271], dye molecules in metamaterials [272, 273], diamond and perovskite nanocrystals in photonic crystals [274, 275].

Previously, our group studied the influence of a 3D photonic band gap on the emission of nanocrystalline quantum dots that were infiltrated as a mobile liquid suspension [35, 159, 179]. Hence, there was no control on the placement of the internal emitters, and the main question “where the emitters reside inside the photonic crystal nanostructure” was addressed indirectly. Therefore, we have embarked on a journey to position emitters at targeted locations immobile in space; moreover, we sought to exploit an independent probe to find the positions of the emitters. Recently, we reported the targeted positioning of nanocrystalline quantum dots inside 3D silicon photonic band gap crystals by means of polymer brush layers that are grafted to the Si-air interfaces using surface-initiated atom transfer radical polymerization (SI-ATRP) [276, 277]. The crystals have the inverse woodpile structure that consists of 2 perpendicular sets of crossing pores (see also Figure 7.3) [213]. We performed high-resolution synchrotron X-ray fluorescence (SXRF) tomography at a high 17 keV photon energy to obtain large penetration depths and efficient excitation of the elements of interest, and unequivocally observed that the quantum dots reside along the axes of the pores [161]. In this chapter we present a detailed optical study of the quantum dots inside the 3D Si photonic band gap crystals and collect emission spectra and excited-state lifetimes. We observe broadband strongly inhibited emission inside the 3D band gap in agreement with theory, as well as enhanced emission above the band gap, as shown in Figure 7.2(b).

7.1.1 Theory

It is well-known in cQED that in the weak-coupling approximation [278] (or Wigner-Weisskopf approximation [279]) spontaneous emission of an excited quantum emitter is precisely described by Fermi’s golden rule [13]. In a modern reformulation [5, 15, 16] the radiative decay rate is linearly proportional to the local density of optical states (LDOS), a classical property that gives the density of vacuum fluctuations, and thus the amount of vacuum noise experienced by a qubit [280]. In a quantum electrodynamical view, vacuum fluctuations stimulate an excited quantum system to decay from its excited state, thereby impeding the quantum functionality that is often available with excited states.¹ The LDOS

¹It is well-known that vacuum fluctuations contribute only one half of the emission rate, the other half being induced by electrodynamic back action, see Refs. [5, 248].

not only controls spontaneous emission and blackbody radiation, but also plays a role in Van der Waals and Casimir dispersion forces between nanoparticles, and in Förster resonant energy transfer (FRET) between different emitters [281].

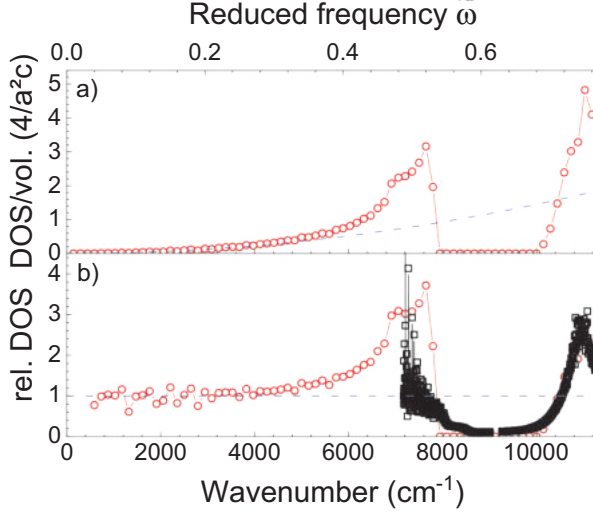


Figure 7.2: (a) Density of states (DOS) computed (red) for an inverse woodpile photonic band gap crystal from silicon ($\epsilon = 11.7$) with pores with reduced radius $R/a = 0.252$. Experiment results are shown for comparison (black squares). The theoretical DOS of a homogeneous medium with the same effective refractive index as the crystal is shown (blue dashed line), and of free space (blue dotted curve). (b) Relative DOS equal to DOS of the crystal over DOS of the effective homogeneous medium. Black squares show our main result, namely the measured intensity of quantum dots inside a 3D silicon photonic crystal normalized to the intensity of similar quantum dots on a silicon surface, and reveal a broad band gap with strong inhibition.

Expressed in words, the LDOS counts the number of electromagnetic field states available for emission, where each state is weighted by its strength at the emitter's position $\mathbf{r}_0$ and the field is projected along the emitter's dipole axis [5, 14, 15]. When averaged over position and orientation, we obtain the density of optical states (DOS).

Since the Bragg length of our photonic band gap crystal ($\ell_{Br} = 300$ nm [282]) is much less than both the size of the unit cell ($a = 680$ nm) and the size of the crystals ($L = 10$ μm), photons emitted by the quantum dots scatter multiple times before being collected, see also Ref. [45]. Therefore, the collected photons are emitted by an ensemble of quantum dots at different positions inside a unit cell and with all orientations of the transition dipole moment. Hence, a suitable interpretation of the experimental observations corresponds to averaging the LDOS over orientations and positions, which is equal to the density of states (DOS) [5].

In Figure 7.2, the theoretical DOS for an inverse woodpile crystal with pores

of reduced radius $R/a = 0.252$ is compared with experimental measurements. Figure 7.2(a) shows the frequency dependence of the DOS that *grosso modo* increases quadratically with frequency.² In the reduced frequency range³ $\tilde{\omega} \equiv a/\lambda = 0.54$ to 0.68 (with a the lattice parameter and λ the wavelength) the DOS is completely inhibited [15, 20, 52, 156, 283–286], which defines the complete 3D photonic band gap. In the photonic band gap, the vacuum fluctuation wavelets bounce off the crystal’s external surface, as portrayed in Figure 7.1. Since the total number of states is conserved, the DOS is enhanced outside the band gap. For comparison, the DOS of a homogeneous medium with the same effective refractive index as the crystal exhibits similar behavior in the low-frequency range to about $\tilde{\omega} = 0.25$, before further increasing quadratically. The DOS of free space is also quadratic, albeit much lower overall than in the effective medium since the DOS is proportional to the (effective) refractive index cubed [5].

Figure 7.2(b) shows the photonic crystal’s relative DOS that is normalized to the DOS of the effective homogeneous medium. This normalization is notably useful for two main reasons: Firstly, it is insightful to remove the parabolic dependence, so that unmodified DOS corresponds to a relative DOS equal to one and enhancements and inhibitions correspond to a relative DOS > 1 and < 1 , respectively. Secondly, such a ratio is a model of experiments as in this chapter, where we normalize the intensity collected from quantum emitters inside a photonic crystal to the intensity of similar emitters in a reference situation without band gap. By such a procedure, we normalize out the specific spectrum of the emitters in order to focus on the crystal properties. Note that similar procedures were used in previous work, where the effect of band gap crystals was studied on laser dye molecules and quantum wells [45, 256]. The black squares show the main result of this manuscript, namely the measurements of one of our 3D silicon photonic band gap crystals with quantum dots as internal quantum emitters. We find a broad range of strongly inhibited emission between about 8000 to 10400 cm^{-1} , characteristic of a 3D photonic band gap with a relative bandwidth (width over center frequency) of about 26%, which matches well with the theoretical relative DOS.

7.2 Materials and methods

7.2.1 3D silicon photonic crystals

We study 3D photonic band gap crystals with the diamond-like inverse woodpile structure that consist of two perpendicular arrays of interpenetrating pores [213]. Our 3D crystals are made from silicon and fabricated with a CMOS-compatible

²The noise-like features, especially in the low frequency region, are the result of binning in frequency space in the process of mode counting. Hence these features are in fact finite-size speckle.

³We express frequency as a reduced frequency $\tilde{\omega} = \omega a/(2\pi c)$, with ω the frequency, a the lattice parameter, and c the speed of light (not to be confused with the lattice parameter in the X, Z directions). The reduced frequency $\tilde{\omega}$ also equals (a/λ) which is convenient in the interpretation of experiments.

process that is described in detail in Refs. [201, 207, 287]. In brief, we use Si beams ($0.5 \times 0.5 \times 10 \text{ mm}^3$) as substrates that are chemically etched to obtain perpendicular crystal surfaces. A thin layer of chromium (50 nm) serves as a hard mask that is deposited on two adjacent surfaces of such a Si beam. Via focused-ion beam writing with Ga ions, we define apertures in an etch mask in a single step on *both* faces into the chromium mask layer. We use deep reactive ion etching using the Bosch process to etch two perpendicular arrays of deep nanopores through the mask apertures into the silicon.

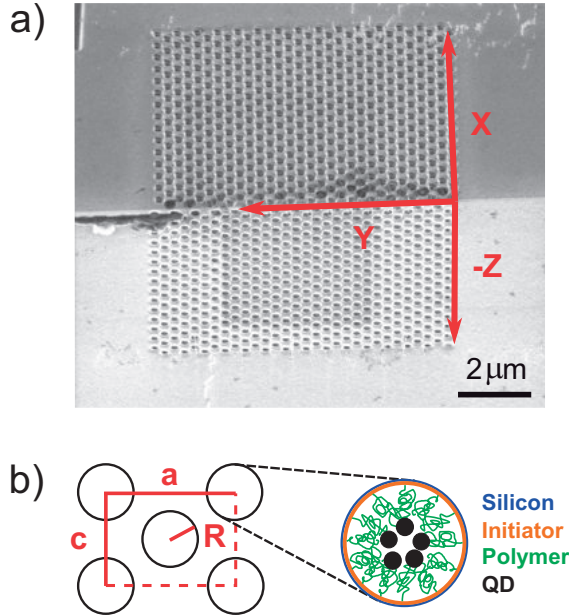


Figure 7.3: (a) Scanning electron micrograph (SEM) of a 3D photonic band gap crystal viewed from 45° on the edge of the silicon beam showing the XY (top) and the YZ surfaces (bottom); the scale bar indicates $2 \mu\text{m}$. (b) View along the pores showing the lattice parameters a , c (with $a = \sqrt{2}c$), and pore radius R . Zoomed-in cross section of one pore with targeted polymer surface-chemistry: ATRP initiator layer (orange), polymer chains forming brushes (green), and covalently attached PbS quantum dots (black) on top of silicon (blue).

Figure 7.3 shows a SEM image of a successfully etched 3D photonic band gap crystal. The pores that enter into the XY surface (top) and into the YZ surface (bottom) mutually cross inside the Si beam and thereby form the 3D tetragonal inverse woodpile structure [232] with a width of about 10 micron that has a broad 3D photonic band gap [213, 225, 288]. The crystals are designed to have a lattice parameter $a = 680 \text{ nm}$ and pore diameters of $d = 260$ or 320 nm . The pore diameters correspond to reduced radii of $R/a = 0.191$ and 0.235 . From Figure 7.2 it is apparent that in this range of pore radii the 3D photonic band gap occurs between 8000 and 10000 cm^{-1} , in the near infrared spectral range, see Refs. [225, 288]. In Table A.4 we present the properties of the silicon photonic

crystals that we etched into the individual silicon beams.

7.2.2 Quantum dots positioned by surface chemistry

As internal emitters, we choose near-infrared emitting lead sulfide quantum dots whose emission band includes telecom bands and is compatible with the transparency range of silicon below the electronic band gap at 1.1 eV corresponding to wavelengths longer than 1100 nm (see, *e.g.*, Ref. [241]). In addition, quantum dots were chosen to have their emission spectrum overlap with the 3D photonic band gap, shown in Figure 7.2.

We analyze three different arrangements of quantum dots as depicted in Figure 7.4: in water suspension, attached to the flat silicon surface and inside a 3D photonic band gap crystal.

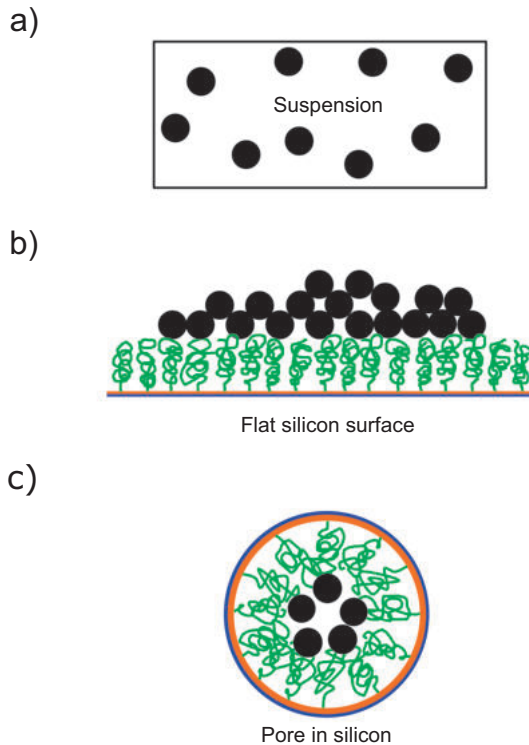


Figure 7.4: Schematic of how quantum dots are likely located in the three different samples studied here. (a) In suspension, the dots have a low density and are well-separated. (b) On a flat Si substrate, the QDs have a high areal density and are likely clustered or aggregated. (c) In a cross section of a crystal pore the QDs have a medium high areal density and are separated thanks to the targeted brush polymer surface chemistry [161].

To position the quantum dots inside the crystals, a thin polymer brush layer

was grafted inside the pores to attach lead sulfide quantum dots, as described in detail in Ref. [161]. The inorganic lead sulfide core of the quantum dots is covered by a poly(ethylene glycol)-amine (PEG-NH₂) ligand that is used to couple to the polymer layer on the silicon photonic crystal, see Chapter 3, Figure 2. Notably, in the process, Cu catalysts are used. Since the quantum dot nanocrystals are much smaller than the photonic crystal pores, it is reasonable to assume the dots do not have a preferred orientation and that their attachment to the brushes is random.

7.2.3 Optical setup

We present here the optical setup used to collect emission from near-IR emitting quantum dots inside 3D silicon photonic band gap crystals, see Figure 7.5 below. Earlier versions of the setup have been reported in Refs. [35, 172, 289]. To excite the quantum dots, we used a pulsed diode laser (PDL, Picoquant: LDH-C 690) emitting at $\lambda = 690$ nm, controlled by a driver (Picoquant: PDL 800-D) with a tunable repetition rate set to 62.5 kHz. The cw power of the pulsed diode laser was measured to be 9.71 mW within the single exciton regime. The lead sulfide quantum dots reside inside the 3D silicon photonic crystal (S) sample that is placed on a three-dimensional piezo stage to align and scan the position of the photonic crystal with respect to the objectives. For time-resolved measurements the sample is excited from the YZ-surface by focusing the incident laser beam with objective O1 (numerical aperture NA = 0.12). Light emitted by quantum dots in the photonic crystal is collected from the XY-face by a high-NA objective O2 (NA = 0.72, Nikon CFIL Plan EPI SLWD). Two separate LEDs and CCDs are used to align both incident and detection foci on the front-face and the side-face of the photonic crystals. All mirrors are silver-coated to provide a high reflectivity in the near-infrared and the visible wavelength ranges.

Light collected from the quantum dots in the photonic crystal is filtered with two longpass filters (Thorlabs KG850 and FEL1100) to remove stray laser light, sent to a grating monochromator (Princeton Instruments, Spectra Pro 2558, gold-coated optics). The monochromator has a turret with two gratings (900 g/mm Holographic for high resolution and 85 g/mm, blazed for 1.35 μ m for low resolution), and a gold mirror to collect all light on one pixel. To record emission spectra, the output of the monochromator is directed to a liquid nitrogen cooled InGaAs line diode array (OMA-V: 1024-2.2 LN). The emission spectra were collected over 600 s integration time.

For time-correlated single photon counting experiments [290], the output of the monochromator is directed to a Peltier-cooled NIR photomultiplier tube (PMT, Hamamatsu H10330-75), equipped with a timing module (Picoquant: PicoHarp 300 counting module). The time-dependent lifetime measurements are integrated over 7200 s duration with a time-bin resolution of 288 ps.

The alignment of the setup is done in three steps: Firstly, a He-Ne laser beam is sent through the holder of the collecting objective O2, by reflecting the incident laser beam with a mirror to align onto the closed entrance slit of the spectrometer. Secondly, the excitation beam from the pulsed laser is aligned and focused onto

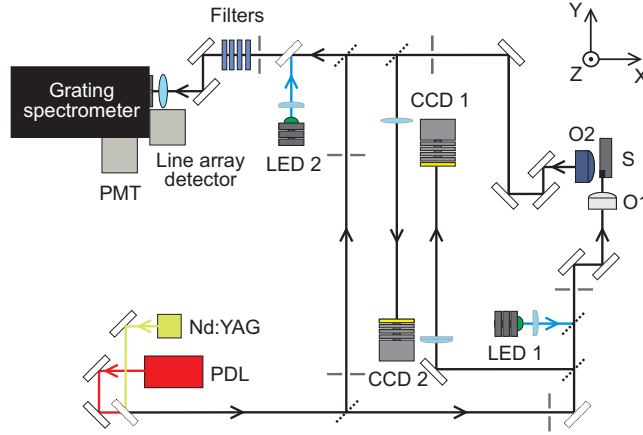


Figure 7.5: Schematic of the optical setup used in this chapter. Two excitation sources were used, a pulsed $\text{Nd}^{3+}:\text{YAG}$ laser ($\lambda = 532 \text{ nm}$) and a pulsed diode laser (PDL, $\lambda = 690 \text{ nm}$). S is the 3D silicon photonic crystal with quantum dots. $O1$ is the objective (numerical aperture $\text{NA} = 0.12$) to focus the excitation light. and $O2$ is the collection objective ($\text{NA} = 0.70$). Two different detectors were used, a PMT (photomultiplier tube) and a line array detector (liquid nitrogen cooled InGaAs). Two sets of LEDs with a CCD are used to image the two sample surfaces where the two individual sets of pores were etched into the silicon.

the YZ surface of the silicon beam. As confirmation, the focus of the laser light is viewed by a CCD camera that is focused onto the same side of the Si beam. The position of the focus spot is chosen such that the laser hits the center of the silicon photonic crystal. Thirdly, the second, XY -crystal surface is aligned in the same way as the first surface by sending the excitation light beam on that face. Since the emission of the near-infrared quantum dots is relatively weak, the signal is at first maximized by using the mirror in the monochromator to collect all counts to one pixel, see also Ref. [172].

7.2.4 Photonic DOS computations

To compute the DOS of the 3D photonic band gap crystals, we have used the plane-wave expansion method [291, 292], implemented in the well-known MPB package [293]. At each wave vector $\mathbf{k}$, the band frequencies $\tilde{\omega}(\mathbf{k})$ are computed. Figure 7.6 shows a resulting photonic band structure, in other words, the band frequencies $\mathbf{k}$ for trajectories in wave vector space between conventional high-symmetry points in the Brillouin zone, the latter being shown in the inset, see also Ref. [282]. Around reduced frequency 0.6, a broad 3D photonic band gap is apparent, that gives rise to the DOS gap in Figure 7.2. By sampling over all points within the Brillouin zone, we obtain the DOS $N(\tilde{\omega})$ at a given frequency $\tilde{\omega}$ as [291]

$$N(\tilde{\omega}) = \lim_{\Delta\tilde{\omega} \rightarrow 0} \frac{Q(\tilde{\omega})}{\Delta\tilde{\omega}}, \quad (7.1)$$

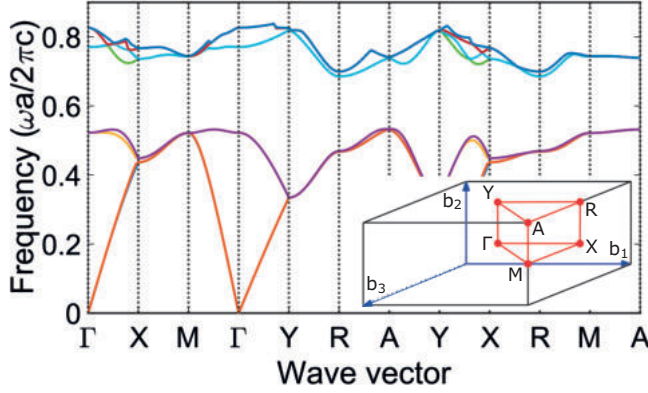


Figure 7.6: Band structure of the 3D inverse woodpile photonic band gap crystal with reduced pore radius $R/a = 0.252$. The inset shows the Brillouin zone of the tetragonal unit cell with marked high-symmetry points and the tetragonal basis vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$.

with $Q(\tilde{\omega})$ the number of states with frequencies in the interval $(\tilde{\omega}, \tilde{\omega} + \Delta\tilde{\omega})$. In the numerical case, frequency is discretized into bins of size $\Delta\tilde{\omega}$ and $Q(\tilde{\omega})$ becomes the number of states $\tilde{\omega}(\mathbf{k})$ found in each bin. The noise-like features in Figure 7.2(b) are well known due to binning in frequency space to count modes [20, 293]. The spatial resolution of the employed tetragonal unit cell is $48 \times 68 \times 48$, corresponding to a cutoff of $N = 156672$ plane waves and the k-space resolution was $32 \times 32 \times 32$ within the Brillouin zone, which was found in previous studies to be a suitable compromise between accuracy and computational time [294].

7.3 Results and discussion

7.3.1 Emission spectra

Figure 7.7 shows emission spectra of the quantum dots in suspension and of quantum dots attached with polymer brushes to the flat silicon substrate adjacent to the photonic crystals. In suspension, the quantum dot emission maximum is observed at 9610 cm^{-1} , which corresponds to a lead sulfide quantum dot diameter of about $D_{\text{size}} = 3.46 \text{ nm}$ [295]. The width is about 1315 cm^{-1} full width at half maximum (FWHM), mostly due to size polydispersity [296], and the maximum intensity is nearly 100 counts/s. The spectra of the quantum dots attached to the silicon surface have a maximum near 8900 cm^{-1} , which is red shifted by about 710 cm^{-1} compared to the dots in suspension. The FWHM of the emission spectra on the surface is about 1070 cm^{-1} , somewhat narrower than in suspension.

We attribute the apparent shift and narrowing to two main qualitative features: firstly, the quantum dots experience different dielectric environments, where the dots in suspension are in water with an optical dielectric function of about $\epsilon_{\text{sus}} = 1.69$ [297]. On the silicon-air surface the dots experience a di-

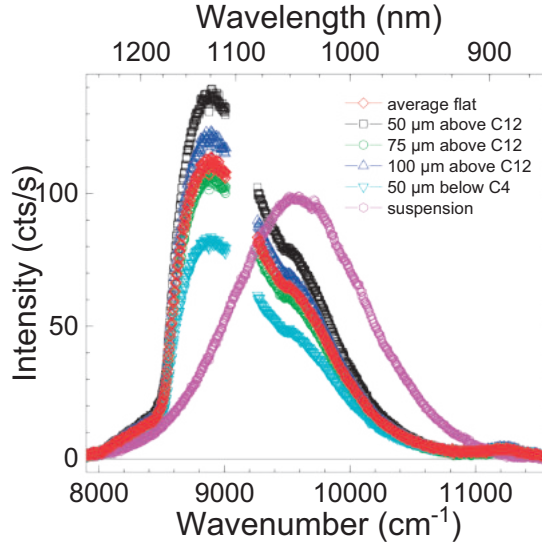


Figure 7.7: The emission spectrum of the PbS quantum dots in suspension is shown as magenta hexagons. The emission spectra of the quantum dots at four locations on the flat silicon surface on silicon beam 1 are shown as black, blue, green and teal symbols, with the average spectrum for the flat surface shown as red diamonds. C4 and C12 are two different crystals on the beam.

electric function $\epsilon_{\text{Si}} = 11.7$ on the Si side and $\epsilon_{\text{air}} = 1$ on the air side, which we interpret as an effective medium with $\epsilon_{\text{med}} = \frac{\epsilon_{\text{Si}} + \epsilon_{\text{air}}}{2} = 6.35$, which is substantially greater than in suspension. In a high-epsilon environment two-level emitters generally emit at a lower emission frequency due to the increased polarization of the environment by the emitting dipole [154, 182], which qualitatively agrees with our observations in Figure 7.7. Secondly, in suspension the quantum dots are well separated whereas on the flat silicon surface they are in close vicinity due to the densification from a 3D chemical reaction environment to a 2D surface. Consequently, we surmise that the dots on the surface experience energy transfer, including Förster Resonant Energy Transfer (FRET) [182, 298], whereas the dots in suspension do not. In case of energy transfer, high-frequency “blue-emitting” quantum dots effectively transfer their excitation to more red-emitting dots, hence the apparent enhancement of the low-frequency part of an emission spectrum at the expense of the high-frequency side. Such an enhancement of the red side and simultaneous decrease of the blue side of the spectrum agrees qualitatively with the observations in Figure 7.7.

Insights into effects of the employed brush surface chemistry are obtained by comparing the emitted intensity collected from different areas on the flat silicon surface, by scanning the excitation laser spot across silicon beam 1, where the length scale of the probe is given by the focal diameter of the excitation laser (about 1 μm). The intensity maxima range from 83 to 139 cts/s, corresponding

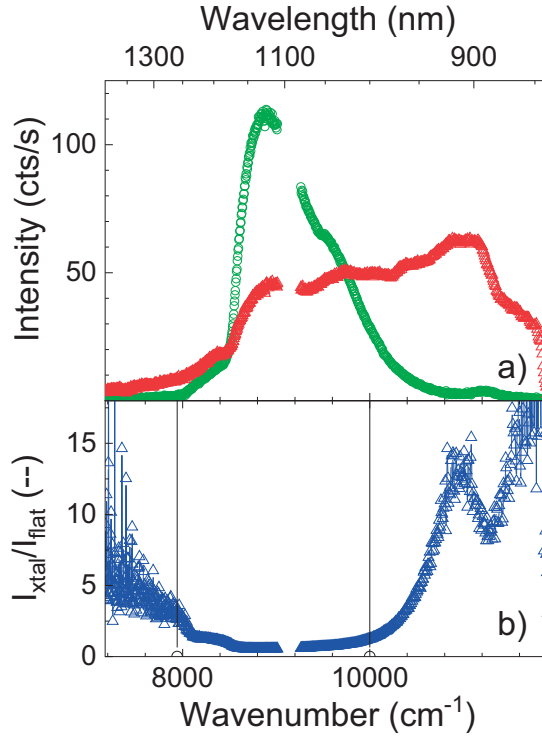


Figure 7.8: (a) Emitted intensity in counts/s versus photon energy (in wavenumbers, bottom abscissa) and wavelength (top abscissa) of quantum dots in crystal 12 (at $Y = 0$) on silicon beam 1 (red triangles). The green circles indicate the average spectrum of quantum dots on a flat silicon surface. (b) Ratio of the crystal spectrum I_{xtal} to reference spectrum on a flat surface I_{flat} (blue triangles). The estimated band gap edges are shown as vertical black lines.

to less than 25% relative change from the average, which is a fairly small variation of absolute intensities, which indicates that the coverage with quantum dots is fairly homogeneous across the silicon surface. This micron-scale homogeneity is attributed to the covalent attachment of the QDs to the polymer brushes that generally leads to a homogeneous and well-controlled coverage. For comparison, on silicon beam 2 the quantum dots were not covalently attached to the polymer layer, but physisorbed. Here, the intensities fluctuate much more while scanning the excitation laser across the sample, namely between 390 and 12600 counts/s (more than 30 times), thus much more than above. We attribute the larger variations to aggregation of quantum dots in patches with few or even many dots clumped together.

Previously, we have probed the location of the quantum dots inside the photonic crystals with high spatial resolution (few tens of nanometers) by synchrotron X-ray fluorescence tomography [161], on the same samples as studied

here, especially silicon beam 1. In the tomography study, we found that the detailed distribution of individual quantum dots shows some inhomogeneity along the length of each pore. However, averaged over the length of pores (several microns) the distribution of quantum dots is highly reproducible and homogeneous, which agrees with the optical probing above. From these observations combined we conclude that the coupling strategy using the brush surface chemistry developed here is a successful one for silicon-based functional samples since the infiltration of the quantum dots into the photonic crystal nanostructures is homogeneous on optically relevant length scales.

Figure 7.8(a) shows the emission spectrum of the quantum dots infiltrated in a 3D photonic band gap crystal and for comparison the spectrum taken on a flat substrate, where the dots were in both cases attached by the same chemical procedure. The spectrum on the flat silicon surface has an emission maximum at 8900 cm^{-1} and a shoulder at 9600 cm^{-1} , as in Figure 7.7. The spectrum of the quantum dots inside the photonic crystal is dramatically modified with respect to the spectrum on the silicon surface (and also compared to the suspension): the emission maximum has shifted to around 11000 cm^{-1} ; in the frequency range around 9000 to 10000 cm^{-1} where quantum dots on Si (and in suspension) show emission maxima, the emission from inside the crystal is strongly inhibited. In addition to different spectral shapes, there are also other remarkable differences in emitted signal: in the frequency window between 8500 and 9750 cm^{-1} the quantum dots in the crystal have a considerably lower count rate; in the low frequency range below 8500 cm^{-1} the quantum dots in the crystal have a similar count rate as on the substrate, and above 9750 cm^{-1} the count rate is greater.

To discern the effect of the crystal on the emission spectrum, we show in Figure 7.8(b) the ratio of the silicon photonic crystal spectrum and the reference spectrum taken on the flat silicon substrate. This relative intensity spectrum shows a broad inhibition range between about 8000 and 10000 cm^{-1} that agrees with the photonic band gap expected from the DOS calculations. At low photon energies, the relative intensity decreases with wave number increasing to the gap. At high photon energies above the gap, the relative intensity increases, showing a marked peak at 10900 cm^{-1} that matches the peak in the DOS spectrum in Figure 7.2(a), and a further increase to 11600 cm^{-1} . While the reference spectrum in Figure 7.8(a) has relatively low count rate in this range, the absolute counts are definitely systematic and significant since they were averaged for 600 s (see Section 7.2.3), thus corresponding to $> 10^3$ cts, which corresponds to $< 0.5\%$ relative error from Poisson statistics. The significance may be further appreciated from the fact that while the ratio in Figure 7.8(b) shows variations, these variations are much less than the overall frequency dependency of the spectra. The relative intensity in Figure 7.8(b) varies up to 15 in the peak at 10800 cm^{-1} , which differs from the relative intensity in the calculated relative DOS in Figure 7.2(b) that equals about 2.5 at the same peak. Several reasonable yet competing explanations for the overall difference in scale factor include: (i) a possible difference in areal density between quantum dots on the flat substrate versus those inside the curved pores, (ii) a possible difference in total number of quantum dots on the flat substrate versus inside the pores (due to different layer thickness), (iii) a

possible difference in optical collection efficiency between the flat substrate (well defined focus) versus the photonic crystal where above-gap excitation light will be strongly scattered [299]. Since it is at this time not possible to conclusively quantify these explanations, we scale each measured relative intensity spectra by a single scale factor such that the peak at 10800 cm^{-1} matches the calculated one, where the resulting factors are listed in Table A.5 of the Appendix.

For the same photonic crystal 12 as probed in Figure 7.8, we performed a position-dependent scan (in the Y direction parallel to the crystal-air interface) to verify that the inhibited emission indeed correlates with the presence of the photonic band gap crystal. The ratio of the intensity of the quantum dots in and near the photonic band gap crystal to the intensity on the substrate far away from the crystal (I_c/I_f) is plotted in Figure 7.9 as a map versus frequency and Y position. Far away from the crystal this ratio closely equals 1 at all frequencies. The emission is observed to be most strongly inhibited at the center of the crystal at $Y = 4 \text{ }\mu\text{m}$, in agreement with recent theoretical position-dependent calculations of the local density of states [53]. The inhibition extends over $10 \text{ }\mu\text{m}$ which is in agreement with the crystal extent shown in Figure 7.3(b).

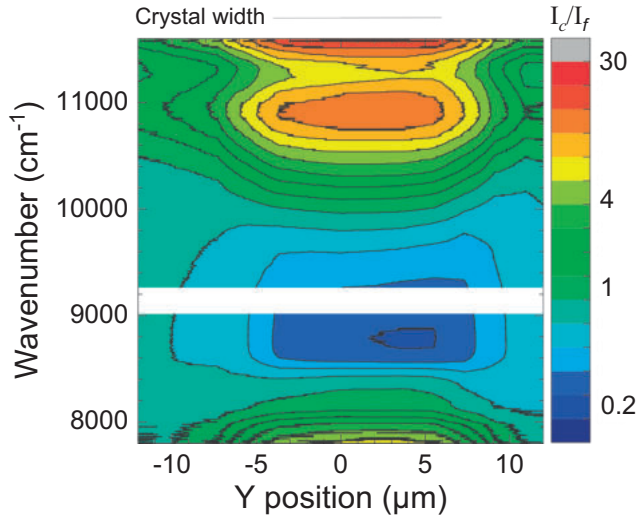


Figure 7.9: Spectral and Y position map of the emission inhibition for quantum dots in crystal 12 on silicon beam 1, obtained from spectra taken at 23 positions. The color map shows the inhibition defined as the ratio of a Y-dependent spectrum taken on the crystal and the flat Si surface reference spectrum (I_c/I_f). Green color ($I_c/I_f \simeq 1$) indicates no inhibition, blue ($I_c/I_f < 1$) is inhibited, and green, orange, red ($I_c/I_f > 1$) are enhanced. The size of the crystal is indicated at the top.

The inhibition smoothly decreases towards the edges of the photonic crystal, due to the finite size of the illuminating pulsed diode laser. In the same Y range where the crystal reveals inhibited emission, there is also a substantial enhanced emission near 11000 cm^{-1} , that matches with the theoretically predicted DOS

peak at reduced frequency $\tilde{\omega} \equiv a/\lambda = 0.76$ in Figure 7.2(a). At both higher wave numbers near 12000 cm^{-1} and lower wave numbers near 7500 cm^{-1} there is additional enhanced emission, but due to the limited emission range of the quantum dots no clear features can be identified that can be compared to the theoretical DOS.

From the major differences between the spectra collected from the crystal versus the one on silicon, it is clear that the 3D photonic band gap crystal has a dramatic influence on the emission of the quantum dots. We discuss several possible hypotheses why the quantum dots reveal a major inhibition in their emission spectra when they are placed inside a 3D photonic band gap crystal, namely (1) a Franz-Keldysh effect, (2) Förster Resonant Energy Transfer (FRET) from quantum dots to the silicon, (3) FRET between the quantum dots, (4) hot-electron transfer from the quantum dots to the silicon backbone, (5) a preferential infiltration of small quantum dots into the crystal pores, and (6) the presence of a 3D photonic gap.

The first hypothesis proposes that the emitted intensity is reduced due to an increased optical absorption, due to a Franz-Keldysh effect whereby the quantum dot's electron and hole wavefunctions increasingly "leak" into their electronic band gap [154, 300, 301]. Firstly, a strong electric field is necessary, which is absent in our experiments; secondly, the increased absorption reported in literature [154] is relatively weak and insufficient to explain a 5 to 30-times inhibition as described below; thirdly, the increased absorption occurs in the intrinsic absorption range of the quantum dots, which occurs at much higher photon energy than the photonic gap. Therefore, this hypothesis is so unlikely that we reject it.

The second hypothesis proposes that the quantum dots reveal FRET to the silicon backbone, as recently reported by Tabernig *et al.* [302]. Firstly, the quantum dots are spaced from the silicon backbone by the polymer brush layer that has a thickness of 30 to 35 nm. While a quantum dot could possibly penetrate into the polymer brush layer, since we aimed for a high density polymer layer, it is unlikely that a quantum dot comes sufficiently close (1 to 10 nm) to the silicon surface to experience FRET. Moreover, the PbS quantum dots have a PEG-shell that further shields FRET. Secondly, FRET is usually associated with a red shifting of emission spectra [182], which is not apparent at all in Figure 7.8(a), on the contrary, the spectra rather appear to show a blue shift for the crystal. Therefore, we find this hypothesis so unlikely that we reject it.

The third hypothesis proposes that the inhibition is caused by FRET between the quantum dots. FRET generally results in a red shift of the emission spectrum. Firstly, if there would be more FRET in the crystal than on the flat substrate, the relative spectrum would reveal a monotonous negative trend, and if there would be less FRET in the crystal, the relative spectrum would reveal a monotonous positive trend. Secondly, the quantum dots have a same chemical environment in the crystals as on the flat reference substrate, hence electron transfer seems equally likely on the reference samples, which corresponds to zero change in the relative intensity spectrum, in contrast to our observations. Neither of the three hypothesized spectral features do not match the observed inhibition, therefore we reject this FRET hypothesis.

The fourth hypothesis proposes that highly excited “hot” electrons inside the quantum dots may be transferred to a semiconductor backbone, see, *e.g.*, Tisdale *et al.* [303]. Since the quantum dots have a similar chemical environment in the crystals as on the substrate, electron transfer seems equally likely on both samples, which corresponds to zero change in the relative intensity spectrum, in contrast to the observed inhibition. Therefore, we reject this hypothesis.

The fifth hypothesis proposes that the smaller quantum dots among the whole size population are preferentially infiltrated into the photonic crystal pores. Firstly, since the crystal pores have a diameter greater than 260 nm, whereas the quantum dots have much smaller diameters of about 3 to 6 nm, it is unlikely that steric effects affect infiltration. Secondly, a preferential infiltration of smaller dots would lead to an effective blueshift of the crystal spectrum compared to the reference, and thus to a relative spectrum with a monotonous positive trend, which does not match the observed inhibition, therefore we reject this hypothesis.

Finally the sixth hypothesis proposes that the strong spectral inhibition is caused by a 3D photonic band gap in the crystal. Indeed a gap is designed to be present in such crystals, see *e.g.* Ref. [288, 304], and below we report further support for this hypothesis, namely that the gap systematically shifts when crystal properties (here, the pore radii) are varied. Therefore, we sustain this hypothesis.

7.3.2 Comparison to photonic DOS

While the observation of a broad and strong inhibition that corresponds to the expected complete 3D photonic band gap in the photonic density of states is at this point remarkable and exciting, it is also surprising in view of our initial expectation that the quantum dots bound to the polymer brushes would have a high quantum efficiency.

From previous work [5, 305, 306] it is known that an important aspect in spontaneous emission control is the extent of the non-radiative decay (with rate Γ_{nonrad}) of the quantum emitter in comparison to the desired radiative decay (with rate Γ_{rad}). This extent is expressed by the quantum efficiency η that is equal to $\eta \equiv \Gamma_{\text{rad}}/\Gamma_{\text{tot}}$, with Γ_{tot} the total emission rate equal to the sum of the radiative and the non-radiative rates $\Gamma_{\text{tot}} = \Gamma_{\text{rad}} + \Gamma_{\text{nonrad}}$. It turns out that these properties decide whether the LDOS is apparent in either cw intensity spectra or in time-resolved observations. From the rate equation, the cw emitted intensity $I(\omega)$ (with spectra as in Figure 7.8 above) is derived to be equal to [305]:

$$I(\omega) = P \frac{\Gamma_{\text{rad}}(\omega)}{\Gamma_{\text{rad}}(\omega) + \Gamma_{\text{nonrad}}(\omega)}, \quad (7.2)$$

where P is the pump rate or excitation rate.⁴ If emitters have a high quantum efficiency near unity ($\eta \simeq 1$) and hence $\Gamma_{\text{rad}} \gg \Gamma_{\text{nonrad}}$, it follows from Eq. 7.2 that nearly every incident pump photon is converted into an emitted photon ($I \simeq P$), hence the emitted intensity is independent of the LDOS. Conversely, if

⁴Since the excitation occurs at a different (much higher) frequency, it is independent of the emission frequency ω .

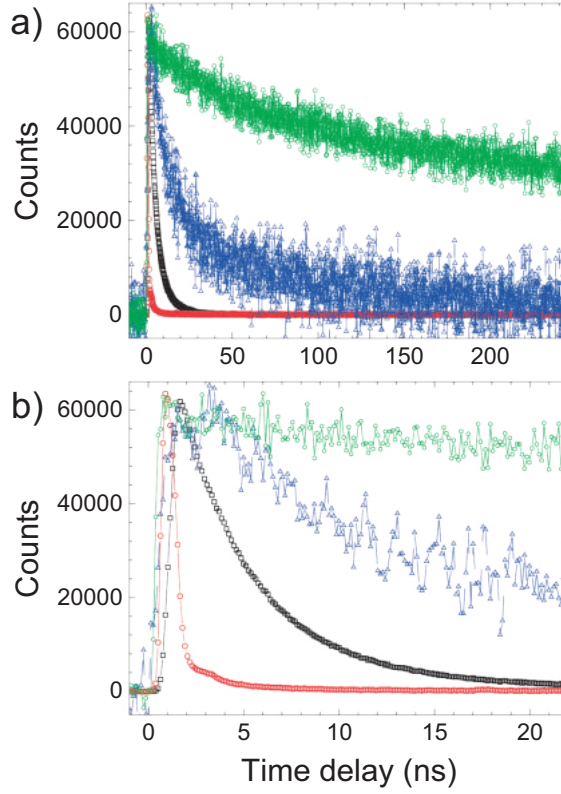


Figure 7.10: Time-correlated single photon counting of PbS quantum dots on a flat substrate on silicon beam 1 (black squares), in crystal 4 (blue triangles), in crystal 12 (red circles), and in suspension (green hexagons, at 1090 nm). Counts per bin are plotted versus photon arrival time. (a) Expanded time scale showing the slow decay in suspension and crystal 4, (b) zoomed-in scale to show the fast decay on the flat substrate and in crystal 12.

the emitters have a low quantum efficiency ($\eta \ll 1$, hence $\Gamma_{\text{rad}} \ll \Gamma_{\text{nonrad}}$), it follows from Eq. 7.2 that the intensity $I(\omega)$ is equal to

$$I(\omega) \simeq P \frac{\Gamma_{\text{rad}}(\omega)}{\Gamma_{\text{nonrad}}(\omega)}, \quad (7.3)$$

which is proportional to the radiative rate, and thus to the LDOS, and this is the regime of our observations here.

To assess whether the quantum dots in our experiment are in the high or low efficiency limits, let us consider their microscopic placement in the various samples, illustrated in Figure 7.4, and time-resolved emission shown in Figure 7.10. In the suspension, the quantum dots have low density (see Figure 7.4(a)), and are manufactured to have as high as possible quantum efficiency. In time-resolved emission in Figure 7.10, the quantum dots in suspension show a decay with an

emission rate of $\Gamma_{\text{tot}} = 0.223 \pm 0.004 \mu\text{s}^{-1}$, which matches well with literature results on good quality PbS quantum dots [295, 307, 308].

When the quantum dots are bound to the silicon substrate or inside the silicon photonic crystal (see Figure 7.4(b, c)), it is reasonable that their local number density is much greater since during the preparation the quantum dots are concentrated from volume to surfaces. Therefore, we expect the quantum dot-quantum dot quenching to be greater, corresponding to a greater non-radiative rate. Moreover, during the preparation the quantum dots are exposed to Cu catalyst that also increases the non-radiative rate [309, 310]. Indeed, in time-resolved emission in Figure 7.10, we observe that the quantum dots inside the 3D photonic crystals and on the substrate show much faster decay than in suspension. On the Si substrate, we find decay rates between $\Gamma_{\text{tot}} = 190.3 \pm 0.6$ and $\Gamma_{\text{tot}} = 267 \pm 0.6 \mu\text{s}^{-1}$, and in the photonic crystal, $\Gamma_{\text{tot}} = 153.0 \pm 1.3 \mu\text{s}^{-1}$, see all data compiled in the Appendix, Table A.6. In other words, the decay rates in and on silicon are about 850 to 1200-fold greater than in suspension, due to a similar major increase of the non-radiative decay rate Γ_{nonrad} .

While one might optimistically speculate that a much faster decay (with an increased decay rate) is caused by an increased DOS, we reject this hypothesis since the fast decay occurs both in the photonic crystal (major DOS modifications, see Figure 7.11) and on the Si substrate where DOS modifications are minor. Since in both cases the non-radiative decay rate is so large, and since this rate is insensitive to the very different photonic DOS of these two different samples, it is reasonable that both samples reveal a similar fast decay. Moreover, the increased total emission rates (see Appendix, Table A.6) *anti-correlate* with the decreasing intensities (see Figure 7.7), which is indicative of quenching. Therefore, we conclude from these observations and from the physico-chemical considerations that the total decay rate Γ_{tot} of the quantum dots on Si and in the photonic crystals is dominated by the non-radiative decay rate Γ_{nonrad} . Therefore, we conclude that the emission spectra as shown in Figure 7.8 are in the low quantum efficiency limit, and hence the observed cw intensity spectra are proportional to the DOS, which we now pursue.

7.3.3 Emission spectra in photonic band gap crystals

Figure 7.11 shows the relative emission spectra of the PbS quantum dots infiltrated in the 3D silicon photonic band gap crystals with two different sets of pore radii, namely in panel (a) crystals with radii $R = 129 \text{ nm}$ (reduced radii $R/a = 0.19$) and in panel (b) with radii $R = 156 \text{ nm}$ (reduced radii $R/a = 0.23$). In this section, we use a two-step normalization. On one hand, the emission spectra of QDots in the crystals are referenced to spectra collected on flat substrates (see Figure 7.8), to normalize out the intrinsic spectrum of the quantum dots and thus concentrate on the spectral shape of the (normalized) local density of states of the crystals. Since the number of quantum dots and the collection efficiencies differ between the photonic crystals and the flat substrates, the count rates between these measurements differ substantially, hence we can unfortunately not calibrate the number of quantum dots between both situations.

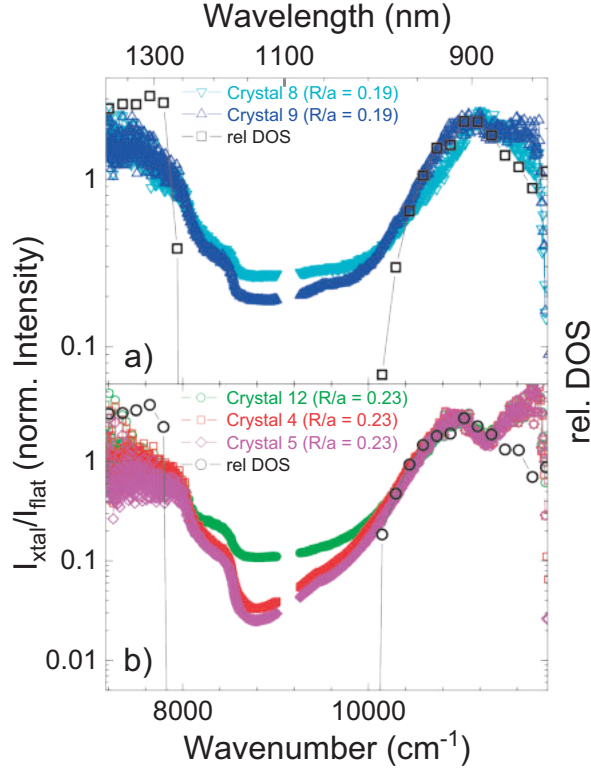


Figure 7.11: Normalized emission spectra of 3D photonic crystals on silicon beam 1: (a) crystal 9 (blue upward triangles), crystal 8 (teal downward triangles), (b) crystal 4 (red squares), crystal 12 (green circles), and crystal 5 (magenta diamonds). The ratio of the spectra measured on the structures and the flat reference spectrum is plotted versus photon energy in wavenumbers, and wavelength (top abscissa). Connected black open symbols are the theoretically calculated relative DOS, for relative pore radii (a) $R/a = 0.19$ and (b) $R/a = 0.23$.

The second step is to normalize relative spectra as in Figure 7.8 to theory as in Figure 7.2(b). An ideal reference is a photonic crystal with a small lattice parameter such that emission occurs in the low-frequency limit below the gap, where such a crystal behaves as an effective homogeneous medium, see Figure 7.2(a) and previous Ref. [305]. Since such crystals were not available during our study (due to the complexity of fabrication, preparation, and X-ray characterization), we propose to use the flat silicon substrate as effective-medium reference sample since it also has a parabolic DOS and a well-defined effective ϵ (see Section 7.3.1 “Emission spectra”). In the thus calibrated relative emission spectra (see Figures 7.8(b) and 7.11), we observe the same characteristic features as in the theoretical spectra, namely the clear peak at 10900 cm^{-1} and of course the major inhibition range. Hence, a relative intensity of 14 in the peak in Figure 7.8 is normalized to correspond to a relative DOS of 3 in Figure 7.2(b). All resulting

normalization constants are listed in the Appendix Table A.5.

In Figure 7.11(a) we see that the relative intensities for two different crystals with pore radii $R = 129$ nm reveal a strong inhibition between about 8000 and 10200 cm^{-1} , in very good mutual agreement. The very good reproducibility confirms that both the photonic crystal fabrication and the quantum dot infiltration method are also well reproduced. The minimum relative emission near 8800 cm^{-1} is about 0.2 to 0.25, corresponding to maximum inhibitions in the photonic band gap of 4 to 5-fold, relative to the reference situation described above. The theoretical DOS has a gap between 8000 and 10200 cm^{-1} , in very good agreement with the observations. Indeed, the (relative) pore radii pertaining to the calculations $R/a = 0.19$ agree well with pore radii derived from the SEM images and the radii used in the sample design.

Figure 7.11(b) shows the relative intensities for three other crystals that all have larger pore radii $R = 320$ nm than the crystals in panel (a). All three crystals reveal strong inhibition between about 8000 and 10400 cm^{-1} , in very good mutual agreement. The inhibition of one crystal (green) amounts to about 10-fold, whereas the other two reveal striking inhibitions up to 30-fold. In view of possible systematic experimental errors like alignment, we estimate the overall inhibition to be 20 ± 10 -fold. The greater inhibition observed for the second set of crystals (in panel (b)) compared to the first makes intuitive sense since the observed inhibition gap is wider. Moreover, the pore radii of the second set of crystals are closer to the value $R/a = 0.245$ that is known to reveal the broadest 3D photonic band gaps in silicon inverse woodpile photonic crystals [225, 311].

Compared to the theoretical DOS, we find that observed enhancement peak near 11000 cm^{-1} in Figure 7.11 matches well in width and shape. A limitation to our interpretation is obviously the use of theory for infinite and perfect crystals, as it predicts zero DOS in the gap that appears to match fairly well on a linear scale as in Figure 7.2, whereas it appears dramatic on a semi-log scale as in Figure 7.11. Similarly, the theoretical DOS just below the gap is higher with a sharp edge, as opposed to the lower and smoother observed edge; the difference is tentatively attributed to fabrication imperfections that are difficult to model. Nevertheless, the theoretical DOS reveals a gap between 7900 and 10200 cm^{-1} , that agrees very well with our observations.

7.4 Summary and outlook

The inhibition in 3D inverse woodpile crystals was previously studied by Leistikow *et al.* in time-resolved studies on high-quantum efficiency quantum dots randomly infiltrated throughout the pores [35]. Leistikow *et al.* observed an inhibition of about 10-fold, which agrees remarkably well with our present results. We speculate that this agreement is coincidental, in view of several notable differences between both studies.

Firstly, in the present study the quantum dots are positioned by the polymer brushes to a limited set of positions in the unit cell (near the axes of the pores, see Figure 7.3(b)), whereas Leistikow *et al.* infiltrated the quantum dots as a

suspension in the pores hence their quantum dots sample all spatial positions in the pores and thus many more positions in the unit cell, namely about 80% of the whole volume. From theory it is known that the local density of states (LDOS) at a single position varies much more strongly with frequency (thus yielding more inhibition) than when such the LDOS is averaged over many more positions inside a photonic crystal's unit cell. In the extreme case of averaging over all position, LDOS becomes the DOS, which yields a smoother result, see Refs. [20, 53].

Secondly, here we study time-averaged emission of low-efficiency quantum dots whereas Leistikow *et al.* studied time-resolved emission of high-efficiency dots; the second technique allows to distinguish between different dynamics in a population of quantum emitters (see van Driel *et al.* [173]), whereas a time-average study reveals an average emission rate. Within a distribution of emission rates that is accessible by time-resolved studies, one may thus find more variable emission rates, whereas averaged rates are usually much smoother.

A third notable difference is that Leistikow *et al.* kept their quantum dots in (toluene) suspension, as a result of which the refractive index ratio with the silicon backbone is less, hence the photonic band gap is narrower, and hence the inhibition is reduced. In the present study, the quantum dots are attached to the brush polymers inside the pores. It is speculated that the overall density of material inside the pores, (see the schematic cross section in Figure 7.3), also increases the dielectric function ϵ inside the pores. This hypothesis is inspired by the observation in our previous X-ray imaging study that tomography (by elastic scattered X-rays) was not feasible due to too little contrast in electron density between the silicon backbone and the filled pores [161]. In summary, compared to the work of Leistikow *et al.*, the reasons above could respectively result in increased, decreased, and similar decay rates, hence the similar observed inhibition seems coincidental to us.

The inhibition of quantum emitters was also studied on completely different 3D photonic crystals [45, 256, 258, 312]. In TiO_2 inverse opal photonic crystals made by self-assembly [313], Koenderink *et al.* observed a broadband angle-integrated inhibition in the emission spectra of laser dye by 5-fold [45, 305]. The inhibition is likely less than observed here in view of the fact that TiO_2 photonic crystals have a lower refractive index contrast than our Si nanostructures, combined with the feature that these inverse opals do not possess a full 3D band gap, as opposed to our photonic crystals. In GaAs woodpile photonic crystals, Ogawa *et al.* reported an inhibition of 45-fold on embedded quantum wells [256]. While the index contrast of GaAs nanostructures is nearly the same as in our Si crystals, the inhibition is slightly larger than observed here, which we attribute to the feature that their emitters are only located in the central layer of the woodpile structure and thus well-shielded, whereas in the present case the emitters are located over the whole length of the pores and thus also near the crystal surface where they are less shielded from the vacuum. Li *et al.* studied PbS quantum dots in polymer photonic crystals and reported an inhibition of 20% [312]. It is reasonable that this inhibition is less than observed here in view of the lower index contrast and concomitant absence of a full photonic band gap. Jorgensen

et al. studied quantum dots in TiO₂ photonic crystals and observed inhibitions of about 4-fold [258], which is also reasonably less than our observations in view of the lower index contrast and concomitant absence of a full photonic band gap. Taken together, all results confirm the long-standing expectation that substantial control of emission of embedded quantum emitters requires nanostructures with high-index semiconductors as backbone, in order to have sufficient refractive index contrast and preferably even a full 3D band gap.

As future extensions of our current study, it will firstly be relevant to calculate the LDOS for the positions where we detected the quantum dots to reside using X-ray imaging. Since it is therefore necessary to introduce X-ray imaging data into numerical *ab initio* computations of Maxwell's equations, it will be relevant to extend the recent method by Corbijn van Willenswaard *et al.* who describe a computational framework to introduce X-ray imaging data into computations [314]. Secondly, to allow for time-resolved studies with quantum dots positioned by brush polymers, it will be important to avoid the steps that induce quenching of the quantum efficiency of the dots. The most important step will be to avoid the copper catalysts, for instance, by invoking copper-free ATRP [315–317]. In addition, it will be relevant to design strategies to shield the quantum dots from oxygen and water, that are also well-known quenchers of highly efficient quantum dots, see *e.g.*, the experimental details in Refs. [159, 179]. Thirdly, the presence of brush polymers offers in future a very exciting prospect, namely to employ the length actuation of the brushes by physico-chemical means [144, 318, 319]. As a result, it may be feasible to tune or even switch the LDOS, the emission rate, and the inhibition by actuating the brushes. This in turn opens prospects to employing such actuated quantum emitters as sensitive position or pH-sensors or as novel platforms for tunable (photo)-chemistry.

CHAPTER 8

Summary and outlook

8.1 Summary

It is well known from quantum mechanics that the control of photonic band gap crystals over the spontaneous emission of embedded quantum emitters - such as semiconductor nanocrystal quantum dots - depends sensitively on where the emitters are located. Therefore, it is an outstanding challenge to derive methods to precisely position emitters inside photonic crystal nanostructures. This thesis takes on this challenge by the use of modern chemical methodologies: we study how to position quantum dots inside photonic band gap crystals with polymer brushes. Therefore, we investigated a suitable surface chemistry *via* silane monolayer formation, polymer brushes, and the covalent attachment of lead sulfide quantum dots with a suitable organic ligand. The knowledge we initially obtained from flat silicon substrates was used as input to derive advanced methods for complex 2D and 3D silicon photonic crystal nanostructures.

We have shown that the polymer must be judiciously chosen in order to control the layer thickness of the grafted polymer brushes on silicon. By choosing poly(*N*-isopropylacrylamide) layers, we achieved a precise control over the layer thickness by varying the activating and de-activating catalyst species. For poly(glycidyl methacrylate) we were able to control the polymer layer thickness by the polymerization time. Since the grafting of poly(glycidyl methacrylate) brushes was more reliable, we decided to proceed with the epoxide-containing polymer.

In order to precisely position the quantum dots within the pores of 3D silicon photonic crystals, it was necessary to develop a sophisticated surface chemistry strategy. Since we made the choice for PGMA layers, a suitable organic ligand on the lead sulfide quantum dots was important. We reacted the epoxide side chains of PGMA with amine-PEGylated lead sulfide quantum dots. By varying the coupling conditions, we achieved densely packed quantum dots attached to PGMA brushes.

Near-infrared emitting quantum dots were studied in this thesis because their emitted photons are not absorbed by the silicon backbone of our 3D photonic band gap crystals. We chose lead sulfide quantum dots for our studies because they are commercially available with various organic ligands. Quantum dot suspensions were studied to measure spectra and time-resolved emission rates of the nanocrystals. We successfully interpreted the decay rates of the lead sulfide quantum dot suspensions with a model for an ideal two-level exciton, as well as an adapted model.

In order to apply the acquired surface chemistry, we had to ensure that the silicon photonic crystals have very clean silicon-air surfaces after the fabrication. Therefore, we had to overcome the problem that after the fabrication of our silicon photonic crystals, fluorocarbon residues are present on the pore walls of the crystals. These contaminations had to be removed by several harsh cleaning steps. Our cleaning procedure, consisting of RCA-2 cleaning and an oxidation step at 800 °C in a furnace, resulted in ultra-clean silicon photonic crystal samples that could be used for the functionalization with quantum dots by means of elaborate surface chemistry.

One highlight of this thesis consists of the experimental observations of quantum dots inside 3D photonic band gap crystals made at the European Synchrotron Radiation Facility (ESRF) in Grenoble. The silicon photonic crystals were analyzed by X-ray tomography to determine the electron density, as described in the PhD thesis of Grishina [206]. We were able to analyze the chemical composition of our crystals using X-ray fluorescence tomography. To the best of our knowledge, our study is the first to obtain experimental data on silicon nanostructures doped with quantum dots whose positions were controlled by polymer brushes. We present the strengths and advantages of X-ray fluorescence tomography compared to other techniques. After a detailed analysis of the acquired data, insights into the quantum dot coverage inside the pores of the photonic crystals were obtained. In addition, we were able to characterize the distinctive bromine atoms of the ATRP initiator molecules and the chlorine atoms of the polymer brushes.

The “*pièce de résistance*” of the thesis consists of optical measurements on our best samples, which were studied by X-ray imaging. The silicon photonic crystal samples were studied in terms of spectra and time-resolved emission of the embedded PbS quantum dots. We observed a record of strongly inhibited emission power in the range of the 3D photonic band gap, in agreement with theory. The successful results were reproduced by emission measurements on different 3D photonic crystals. The decay rates of quantum dots positioned in photonic crystals were lower than those of dots positioned on a flat polymer layer outside the crystal on flat silicon. Compared to suspensions, the decay rates were very fast and we estimate very low quantum efficiencies of the dots positioned in the photonic crystals. Our results open up new avenues for functionalizing the sample architecture to create novel types of organic solar cells with high efficiencies.

8.2 Outlook

We discuss in this section research projects that build on the scientific results presented in this PhD thesis. The projects include how to improve the sample fabrication and the properties of future surface-functionalized 3D photonic band gap crystals. Improvements range from actuation of the polymer brushes by stimuli, to avoiding the quenching of the quantum dot emission.

8.2.1 Control and actuation

A next logical research step beyond our study is to increase and vary the polymer layer thickness while keeping the structural parameters of the photonic crystal the same. With this approach it will be possible to track how the quantum dot position is controlled by the polymer layer by monitoring the quantum dot emission spectra and lifetime in samples with controlled variable brush thickness. An exciting subsequent step would consist of actuating the polymer layer. Actuation of a polymer layer has already been demonstrated by temperature responsive polymer brushes, *e.g.*, with a lower or upper critical solution temperature (LCST), resp. (UCST) as for poly(*N*-isopropylacrylamide) (polymer layer kinetics studied in Chapter 2) [92, 320, 321]. Active photonic band gap crystals with quantum dots on actuated polymers open the opportunity of realizing fully reversibly switchable emitters, even controllable from inhibited to enhanced.

8.2.2 Improvements for the chemical synthesis

In Chapter 7 we realized that the QDot emission is quenched by catalyst residues that were still present after the synthesis. To solve this problem and achieve high quantum efficiency quantum dots, we propose to change the reaction scheme used for the polymers grafts in Chapter 3. In particular, it will be important to avoid Cu(I) and Cu(II) as catalysts, to avoid quenching of the QDots. Thereby one retains a high quantum efficiency of the QDots, so that true control of the emission rate is obtained, and especially also the excited-state population of QDots will be obtained which puts us in an exciting starting point to explore novel photonic chemistry (see, *e.g.*, Refs. [35, 159]).

8.2.3 Characterization and Imaging

To further improve the outcome after the volume reconstruction, it will be crucial to measure a complete structure with a resolution of 20 nm or below. An alternative to SXRF is FIB tomography that employs use of SEM images taken from different slices of an actual 3D photonic crystal that is being cut by focused ion beam (FIB). With a voxel thickness of 10 nm its resolution is comparable to SXRF and can be further improved up to 5 nm in *X* and *Y* and even less for smaller structures. It is inspiring that the first results have already been taken by Goodwin *et al.*, in a collaboration between COPS and MESA+ Nanolab. Elemental mapping by EDX is in addition also available, although low-*Z* lighter elements are more difficult to detect, similar to synchrotron tomography. The data analysis is much easier than the volume reconstruction of SXRF and is done in-house, but the analysis is destructive, and thus the sample cannot be measured optically anymore after the FIB tomography characterization.

8.2.4 Distance-dependent spectroscopy

As mentioned in Section 8.2.1 it will be crucial to further study the effect of the thickness and density of the polymer brush layer on the quantum dots. Both the

thickness and the density of the brush layer will strongly influence the resulting emission from the emitters since the distance of the QDots to the silicon will vary and thus the chemical environment of the QDots. Our studies in Chapter 7 indicate that the emission spectra and lifetimes of lead sulfide quantum dots attached to 30-40 nm polymer brushes change significantly compared to quantum dots in suspension. An optimized polymer layer thickness in the range of 80-120 nm will be highly interesting for implementation into 3D photonic band gap crystals with pore diameters of 320 nm. For instance, preliminary studies by summer interns with alternating layers of poly-L-lysine (PLL) and polystyrene sulfonate (PSS) polymers have yielded promising results in this direction. To characterize interesting substrates and photonic crystal samples, a suitable distance-dependent characterization method will be implemented.

8.2.5 Spontaneous emission control and its applications

As extensions of our current emission studies described in Chapter 7, it will firstly be relevant to calculate the LDOS for the positions where we detected the quantum dots to reside using X-ray imaging. Since it is therefore necessary to introduce X-ray imaging data into numerical *ab initio* computations of Maxwell's equations, it will be relevant to extend the recent method by Corbijn van Wilenswaard *et al.* who describe a computational seminal framework to introduce X-ray imaging data into computations [314]. Secondly, to allow for time-resolved studies with quantum dots positioned by brush polymers, it will be important to avoid the steps that induce quenching of the quantum efficiency of the dots (see above). The most important step will be to avoid the copper catalysts, for instance, by invoking copper-free ATRP [315, 316, 322]. In addition, it will be relevant to design strategies to shield the quantum dots from oxygen and water, that are also well-known quenchers of highly efficient quantum dots, see *e.g.*, the experimental details in Refs. [159, 179]. Thirdly, the presence of brush polymers offers in future a very exciting prospect, namely to employ the length actuation of the brushes by physico-chemical means [144, 318, 319, 323]. As a result, it may be feasible to tune or even switch the LDOS, the emission rate, and the inhibition by actuating the brushes. This in turn opens prospects to employing such actuated quantum emitters as sensitive position or pH-sensors or as novel platforms for tunable (photo)-chemistry.

Appendices

A X-ray fluorescence tomography

In this Appendix we present a schematic for the measurements of the projection maps by Radon transform. We show the measured resolution of the setup for the horizontal and the vertical direction. We show additional data for the projection maps for chlorine, chromium, copper bromine, gallium, and lead for completeness at this stage of discussion. The given atom densities are not corrected for self absorption. The correction factors can be found in the section of the volume reconstruction part c) in Section 6.2.2.

A.1 Projected X-ray fluorescence and backprojection

To provide a didactic introduction in X-ray fluorescence imaging, we show in Figure A.1(a) a 2D free form object with a density distribution $f(x, y)$ for a certain element l . In Figure A.1(b) the X-ray beam traverses the object and excites the atoms of species l along the beam path. Each photon emitted along the beam path is detected by the fluorescence detector from different positions within the sample volume. The detector thus sees a sum of the intensities for a certain X-ray beam position s and sample orientation θ . The projection shown on the right of Figure A.1(b) is the result of a X-ray beam that traverses trough the sample at different positions s by rotating the sample.

Figure A.2 shows the backprojection of the projections $P(s, \theta)$. The object is reconstructed from the complete dataset consisting of values for $P(s, \theta)$ at different locations (raster scan). After the backprojection a blurred object is obtained. The backprojections are done along all lines of response (LORs) at a fixed θ . The knowledge where the values came from was lost in the projection step. A constant value of $P(s, \theta)$ is placed back into the position of the appropriate LOR.

Figure A.3 shows the projection and the following backprojection for a didactic example provided by Zvolský [324]. Figure A.3(a) shows the projections of an object with the information in four sub volumes a, b, c and d. In this step the information is projected angle-dependent onto the detectors. We show four different detectors (blue) in this example that measure at four different angles, two detectors with two pixels, and two detectors with three pixels. For instance the two-pixel detector in the down ward direction sees on one summed sub volume (a+c) and on second sub summed volume (b+d). Figure A.3(b) presents the backprojections of the projections to obtain the unknown object. Here the information that previously arrived at the detector is send back to the object along all LORs. For example the informations (a+c) and (b+d) are sent back

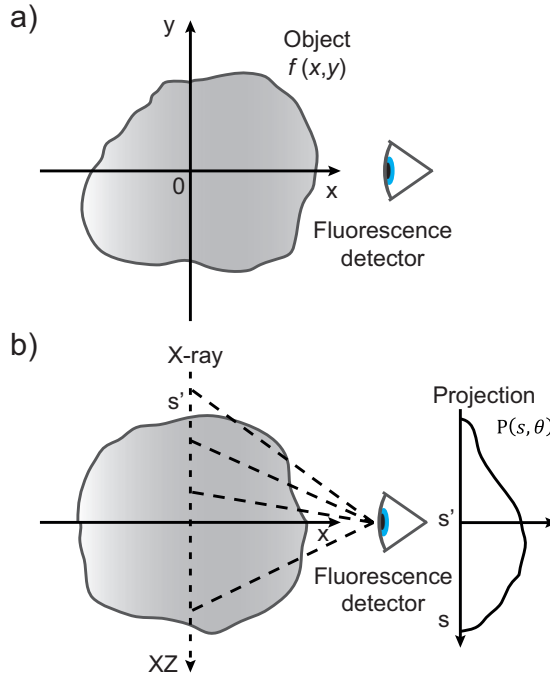


Figure A.1: Schematic for the measurement of the projection maps in X-ray fluorescence: a) 2D density function of object $f(x, y)$ for elemental species l , b) when a X-ray beam is incident at position s' in the Y -direction, it excites all atoms along its path, that will emit to the detector (right). Right inset: cross section of the density projected along (s, θ) that is scanned in the measurements.

reverse along the two individual LORs. Figure A.3(c) shows the result of the backprojections. The result of all LORs are the sum of all informations collected in step a). In Figure A.3(d) the projection sum is subtracted from each entry. The projection sum for this didactic example is the sum $(a+b+c+d)$. From the left top pixel (a), from Figure A.3(a), $(a+b+c+d)$ is subtracted. Figure A.3(e) presents the result of the subtraction. Figure A.3(f) shows the final result. The results from Figure A.3(e) are divided by the common factor $N - 1 = 3$ (where the number of sub volumes equals $N = 4$).

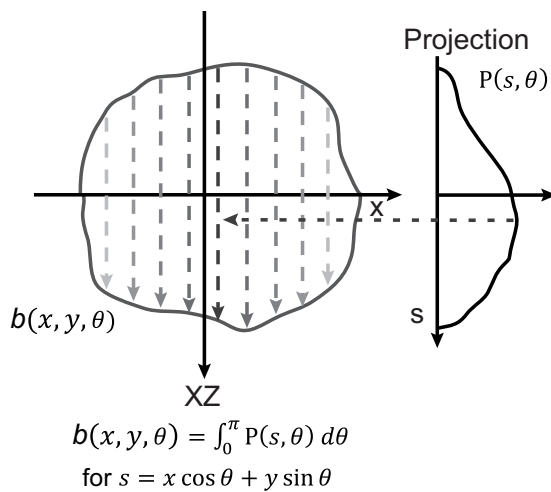


Figure A.2: Schematic for the backprojection of the projection maps to reconstruct the object.

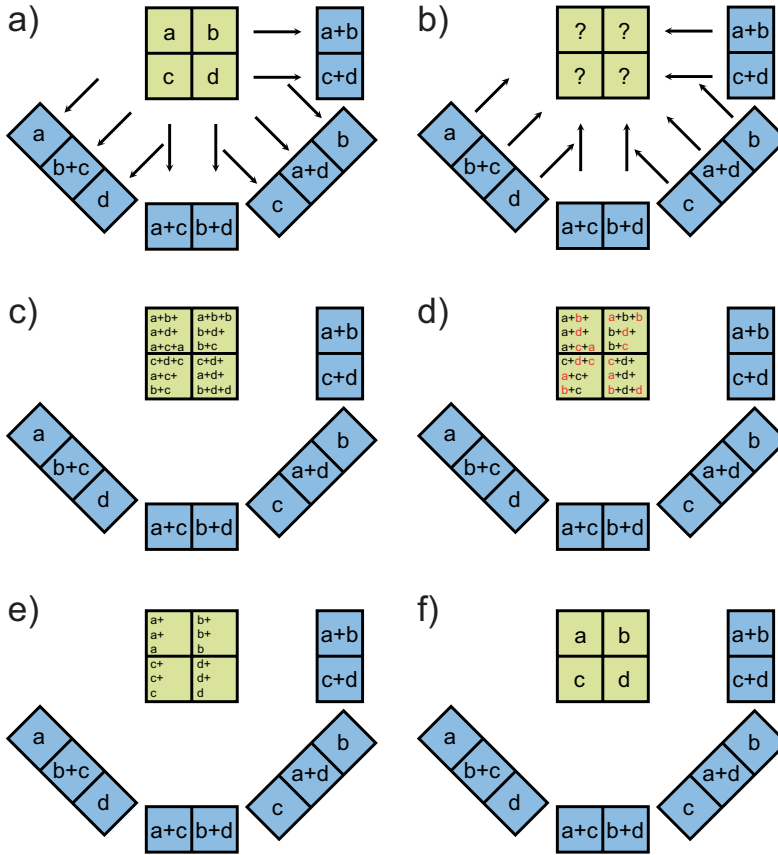


Figure A.3: Schematic for the projection and backprojection for a simplified object (green) consisting of four sub volumes a,b,c and d. Adapted from Ref. [324]. a) In four orientations a traversing X-ray beam reveals four different sets of observations on a simple pixel detector (blue). b) In backprojection, we want to reconstruct the unknown object from the measured data, c) In a first step, all intensities are summed in the corresponding sample part. d) The common terms in each sample part are identified, e) and are subtracted. f) Dividing all densities by the common multiplier (here: 3) yields the original density distribution.

A.2 Samples

In Tables A.1 and A.2 we present an overview of the studied samples.

Table A.1: Properties of the photonic crystals 3DPC1 and 3DPC2 studied by X-ray fluorescence tomography. The column "Sample and structure name in the text" gives the sample name abbreviation that was used in the text, column "Sample name in the lab" the sample name used in our group and "Remarks" further details on the photonic crystals.

Sample and structure name in the text	Sample name in the lab	Remarks
3DPC1	PG-EBAR-30032017-CH4B, Structure 12	3D photonic crystal sample fabricated with the single-step etch mask process [206, 207] in March 2017. Structure is quasi-perfect without embedded defects. Design: $R = 160$ nm and $a = 686$ nm. 3D structure is surrounded by bulk silicon. From the fitted dataset we obtained the areal mass density which we converted into areal and volume atomic densities for each species. The photonic crystal volume was reconstructed and drift-corrected.
3DPC2	PG-EBAR-30032017-CH3B, Structure 1	3D photonic crystal sample fabricated with the single-step etch mask process in March 2017. Structure is quasi-perfect without embedded defects. Design: $R = 160$ nm and $a = 686$ nm. 3D structure is surrounded by bulk silicon. From the fitted dataset we obtained the areal mass density which we converted into areal and volume atomic densities for each species. The photonic crystal volume was not reconstructed yet due to incomplete drift-corrections.

Table A.2: Properties of the photonic crystal 3DPC3 studied by X-ray fluorescence tomography. The column "Sample and structure name in the text" gives the sample name abbreviation that was used in the text, column "Sample name in the lab" the sample name used in our group and "Remarks" further details on the photonic crystal.

Sample and structure name in the text	Sample name in the lab	Remarks
3DPC3	PG-10062016-EBAR-CH02, Structure 10	3D photonic crystal sample fabricated with the single-step etch mask process in June 2016. Structure contains a line defect at row 3. Design: $R = 150$ nm and $a = 750$ nm. 3D structure is surrounded by bulk silicon. From the fitted dataset we obtained the areal mass density which we converted into areal and volume atomic densities for each species. The photonic crystal volume was not yet reconstructed due to surface contaminations in the field of view.

A.3 Raw data

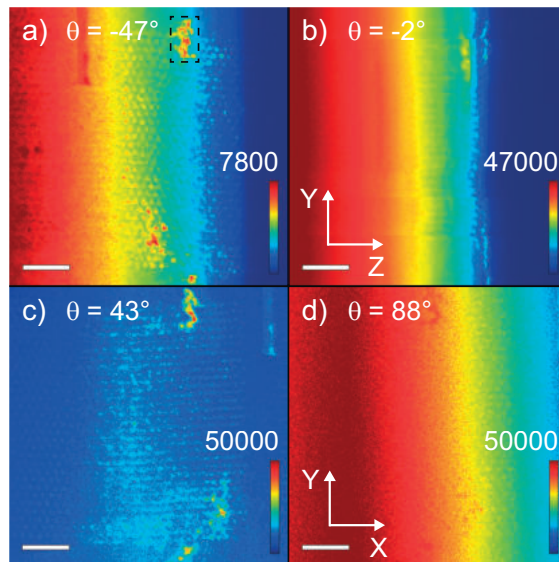


Figure A.4: Intensities $I(x, y, \theta)$ measured for 3DPC1, summed over all energies E for four orientations: a) $\theta = -47^\circ$, b) $\theta = -2^\circ$, c) $\theta = 43^\circ$, d) $\theta = 88^\circ$. In each panel the color bar shows the counts. The size of each panel is 240×240 pixels, corresponding to $12 \times 12 \mu\text{m}^2$. The scale bar corresponds to $2 \mu\text{m}$.

Figure A.4 shows the total intensities $I(x, y, \theta)$ recorded while scanning the (x, y) position of 3DPC1 at four representative angles θ . These scans represent what one observes during the synchrotron run. The total intensities $I(x, y, \theta)$ are summed over all energies E

$$I(x, y, \theta) = \sum_i I(x, y, \theta, E_i). \quad (= \text{cts/area}) \quad (\text{A.1})$$

Figure A.4(a) shows the total intensity at $\theta = -47^\circ$ (corresponds to Figure 6.4(a)). Tending from right to left, the signal is zero since the X-ray beam is in vacuum right of the Si bar, the signal becomes non-zero at about 1/6th from the right indicating the vertical edge of the Si bar. The signal gradually increases towards the left since the exciting X-ray beam traverses increasingly more material. Within the Si bar, the intensity reveals a faint periodicity in both the low intensity range (right) and the high intensity range (left). At the top of the image, about 1/3rd from the right (dashed black rectangle), there is an elongated vertical structure that we will show later in the discussion to be a small region of unrinsed catalyst (containing Cu, Br and Cl) on the sample surface.

Figure A.4(b) shows the total intensity at $\theta = -2^\circ$ (corresponding cartoon in Figure 6.4(b)). The edge of the silicon bar is clearly visible at about 1/4th from the right, and hence the fluorescence quickly increases to its maximum since the

exciting X-ray beam traverses nearly a constant amount of material. The maximum intensity of 50000 is clearly higher than in Figure A.4(a), since the exciting X-ray beam traverses much more material than at -47° . The horizontal streaks in Figure A.4(b) reveal that the sample slightly moved during this scan. Subsequently, we corrected for these shifts before performing the volume reconstruction of the sample. The periodic structure of the photonic crystal is faintly visible at the edge of the bar, conversely in the bulk of the bar the 3D periodicity is washed out by the averaging of the fluorescence along the X-ray beam direction.

Figure A.4(c) shows the total intensity at $\theta = 43^\circ$ (corresponds to Figure 6.4(c)) that shows the periodic structure more clearly. Higher intensities were observed in small areas on top of the silicon. Furthermore it is overall observed that the intensity is not homogeneous throughout the whole sample. At the right top of Figure A.4(c) the elbow-shaped marker is seen close to the photonic structure. At the top a contamination is observed with a "s-shape" most likely consisting of catalyst residue.

Figure A.4(d) shows the total intensity at $\theta = 88^\circ$ (corresponds to Figure 6.4(d)). The edge is pointing vertical at about 1/4th from the left which is not visible here. The red area seen in Figure A.5(d) is caused by the fact that the beam is just touching the sample under an shallow angle, hence the X-ray beam travels through the whole silicon bar which leads to high detector counts. We observe a faint periodicity in the red band. The elbow-shaped marker is visible at the top right corner of the image. At the top center the contamination with the "s-shape" is visible. To proceed further with data analysis, we now turn to energy-resolved data in order to identify the elements.

A.4 Elemental identification

Figure 6.4 shows an energy-resolved X-ray fluorescence spectrum that is averaged over all 240×240 pixels in the image shown in Fig.A.4(a) where $\theta = -47^\circ$:

$$I(E, \theta) = \sum_{i,j=1}^{240} I(x_i, y_j, E, \theta) \quad (= cts) \quad (\text{A.2})$$

where E is the photon energy equal to $E = \hbar\omega$ in keV units. The spectrum is typical for all studied orientations. The peak at 1.74 keV is the Si-K transition from the photonic crystal matrix, and the peak at 17 keV is the excitation by the incident X-ray beam. The excitation peak is broadened compared to the narrowband incident X-rays as a result of the contributions of firstly, the elastic scattering and the resulting broad Compton peak (tail to lower energies), and secondly, by the resolution of the silicon detectors (resolution of 130 eV at 5 keV).

In the X-ray spectrum in Figure 6.4b) we identify the involved elements from their known transition energies, as constrained by our know-how of the involved chemical compounds during the sample preparation. We conclude that the following elements are present: bromine, chlorine, chromium, copper, gallium, and lead. In order of increasing photon energy, we observe the following elemental transitions in Figure 6.4b).

Chlorine is present since it is in the Cu(I)Cl catalyst species used in the polymerization and chlorine is the terminating group of the polymer brushes. Chlorine reveals characteristic $K_{\alpha 1}$ and $K_{\alpha 2}$ lines at 2.622 keV and 2.621 keV that appear as a single averaged line at 2.62 keV. In addition, there is a faint K_{β} line at 2.82 keV that is partly overlapped by a Pb M-line (see below). The chlorine signal is relatively weak compared to the other signals, revealing only a few times 10^4 counts.

Chromium is present in the sample as the hard-mask material for the deep reactive-ion etching of the pores that define the 3D photonic crystal. The chromium $K_{\alpha 1}$ and $K_{\alpha 2}$ lines at 5.415 keV and 5.406 keV appear as an averaged K_{α} line at 5.41 keV. Moreover, we observe the chromium K_{β} line at 5.95 keV. The chromium signal is relatively weak, revealing only a few times 10^4 counts.

Ga is present in the sample since it has been used to write the etch mask by means of focused-ion beam milling. The gallium $K_{\alpha 1}$ and $K_{\alpha 2}$ line at 9.252 keV and 9.225 keV appear as an averaged K_{α} line at 9.24 keV. In addition there is a gallium K_{β} line at 10.26 keV.

Bromine is characteristic for the ATRP-initiator monolayer for the brush synthesis, and it is also present in the Cu(II)Br₂ catalyst species. The bromine K_{α} lines (α_1 and α_2) are occur at 11.924 keV and 11.878 keV. Since these two transition lines are closely spaced the individual K_{α} lines cannot be resolved, but instead an averaged K_{α} line can be observed at 11.91 keV. In addition we determine a bromine K_{β} line (β_1) at 13.29 keV.

Lead is present in the PbS quantum dots and reveals fluorescence at an energy of 10.552 keV and 10.450 keV for L_{α} lines (α_1 and α_2). Since these two transition lines are very close to each other the individual L_{α} lines cannot be resolved, but an averaged L_{α} line can be observed at 10.55 keV. At 9.19 keV the escape peak from the L_{α} emission lines is observed. The lower energy can be explained by the energy loss due to absorption of the fluorescent into the bulk silicon of the SDD. In addition lead L_{β} lines (β_1 and β_2) at 12.614 keV and 12.623 keV are observed. Since these two transition lines are very closely spaced the individual L_{β} lines cannot be resolved, but an averaged L_{β} line can be observed at 12.62 keV. Additionally an escape peak at 11.35 keV from the lead L_{β} lines is observed. Furthermore a lead L_{γ} line (γ_1) at 14.76 keV is observed. Interestingly another lead peak is present at 15.18 keV that is a sum of the L_1N_2 , and L_2O_4 transitions.

Copper is introduced by the two catalyst species Cu(I)Cl and Cu(II)Br₂, and the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines occur at 8.048 keV and 8.028 keV, respectively. Since the two K_{α} emission lines are very close to each other they cannot be resolved, and an averaged K_{α} line is observed at 8.04 keV. Moreover, the copper K_{β} line (β_1) is observed at 8.91 keV.

A.5 Angle-dependent atomic areal densities

From the fitted dataset in Figure 6.4b) we obtain the areal mass density $\rho_{a,l}$ (in units ng/mm^2) with the help of the ESRF PyMCA software. The use of a calibration sample with a known areal mass density for different elements was crucial to determine the sensitivity of the two detectors. The calibration fac-

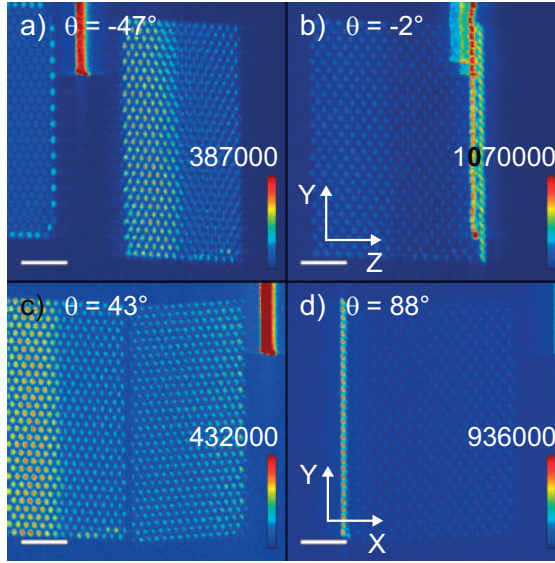


Figure A.5: Projection maps of the number of Ga atoms per pixel area (50×50 nm) and integrated along the propagation direction of the beam, for sample orientations: a) $\theta = -47^\circ$, b) $\theta = -2^\circ$, c) $\theta = 43^\circ$, d) $\theta = 88^\circ$. The signal is an average of the Ga K_α and the Ga K_β line (see Figure 6.4b)). Color bars with the scales are given in each panel. The scale bar represents 40 pixels ($2 \mu\text{m}$).

tor was taken into account for the calculation of the areal mass density. The areal mass densities $\rho_{a,l}$ we convert into areal atomic densities $N_{a,l}$ (in units atoms/pixel area) for each species l with

$$N_{a,l} = \frac{(\rho_{a,l})MS^2N_A}{u_l}, \quad (= \text{atoms/pixelareasampleddepth}) \quad (\text{A.3})$$

where M is the conversion from ng to g, S the spatial resolution per pixel ($S = 50$ nm), u_l the atomic mass, and N_A the Avogadro constant. In this section we discuss projection maps that are taken from the fitted data set. Each pixel in such a map represents the total amount of material per pixel area and per volume of the sample that is traversed by the X-ray beam at the angle θ . We discuss here mainly data for 3DPC1. Similar data were collected for structure 2 and for structure 3.

First, the areal densities for gallium are presented. Gallium is presented first because it marks the pore entrances and thus the surface where the 3D photonic crystal is located on the silicon bar. Figure A.5 shows projection maps of the number of Ga atoms per pixel integrated along the sample depth at four different orientations θ . Figure A.5(a) shows the projection at $\theta = -47^\circ$. The orientation of the silicon bar to the X-ray beam is shown in Figure 6.4(a). On the right we observe the 3D structure by viewing through the surface of the YZ plane first and then through the surface of the XY plane behind. Half of the structure

on the YZ plane shows a higher intensity for Ga. The elbow-shaped marker is visible at the top left (red). At the left we observe a second structure (2D) which was etched in one direction along Z deeper on the XY plane.

In Figure A.5(b) we observe the structure from a high-symmetry angle along the X -axis onto the YZ plane (compare to Figure 6.4(b)). Tending from left to right in the area where the pores are visible, we obtain a higher intensity for Ga for smaller Z -values halfway up towards the edge of the structure. About half of the YZ surface of the structure shows a higher Ga density. At about 1/3th from the right the two elbow-shaped markers from two structures almost overlap each other. The high intensity represents the Ga atoms on the XY surface.

Figure A.5(c) shows the YZ surface on the left and the XY surface on the right (compare Figure 6.4(c)). The gap in between is the edge of the silicon bar. The projection confirms that half of the YZ surface shows a higher atomic density for Ga on the left side (smaller Z -values). The marker is visible on the top right.

In Figure A.5(d) we observe the XY surface which shows lower atomic densities than the YZ plane in Figure A.5(b) (compare to Figure 6.4(d)). The intensities on the XY surface are more homogeneous than on the YZ surface. On the left side the edge and the gallium signal that originates from the YZ surface is visible. The marker is present at the top right corner. With the help of the gallium signal as a surface marker of the 3D photonic crystal and its surrounding structures, it is now easier to understand the positions of the other elements presented below.

Figure A.6 shows projection maps of the number of Cr atoms per pixel integrated along the sample depth at four different orientations θ . Chromium is present on top of our silicon bars since we used chromium as a hard mask to etch the pores of the photonic crystal. Figure A.6(a) shows the projection at $\theta = -47^\circ$. On the right we observe the 3D structure by viewing through the YZ plane first and then through the XY plane. Half of the structure on the YZ plane shows a higher intensity for Cr, as with Ga. The elbow-shaped marker is slightly visible at the top left. To the left we observe the second 2D structure that was etched in one direction along Z further on on the XY plane.

In Figure A.6(b) we observe the structure from a high-symmetry angle along the X -axis. Tending from left to right, we obtain a higher intensity for Cr for smaller Z -values halfway up towards the edge of the structure. Half of the YZ surface of the 3D photonic crystal structure shows a higher Cr atomic areal density. At about 1/3th from the right the two XY surfaces from the 2D and the 3D structure almost overlap with each other. The high intensity represents the Cr atoms along the X -axis on the XY surface.

Figure A.6(c) shows the YZ surface on the left and the XY surface on the right. The projection confirms that half of the YZ surface shows a higher atomic density for Cr on the left side (smaller Z -values). The marker is slightly visible on the top right.

In Figure A.6(d) we observe the XY surface which shows lower atomic densities than the YZ plane in Figure A.6(b). The intensities on the XY surface is more homogeneous than on the YZ plane. On the left side the edge and the YZ surface are visible.

We conclude that chromium is still present on our silicon bar even after our

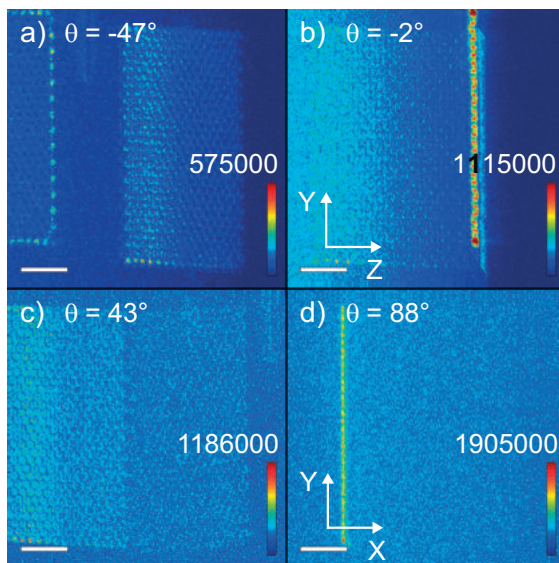


Figure A.6: Projection maps of the number of Cr atoms per pixel area ($50 \times 50 \text{ nm}^2$) and integrated along the propagation direction of the beam, for sample orientations: a) $\theta = -47^\circ$, b) $\theta = -2^\circ$, c) $\theta = 43^\circ$, d) $\theta = 88^\circ$. The signal is an average of the Cr K_α lines at 5.41 keV and of the Cr K_β line at 5.95 keV (see Figure 6.4b)). Color bars with the scales are given in each panel. The scale bar represents 40 pixels ($2 \mu\text{m}$).

cleaning procedure. On the YZ surface the chromium contamination is higher.

As the next element we discuss in Figure A.7 chlorine that is characteristic for the brush layer since chlorine is the terminating group of the polymer brushes. The chlorine-based catalyst CuCl that was used in the polymerization makes the interpretations more difficult. The catalyst should have been completely removed during the process but is still present on the sample surface. Figure A.7(a) shows the projection at $\theta = -47^\circ$. It appears that the Cl signal from inside the photonic crystal is weak. On the right we observe the 3D structure by viewing through the YZ plane. The periodicity of the pores is faintly visible. Chlorine is present throughout the pores of the photonic crystal which is the first indication of the presence of a polymer brush layer. The projection maps for chlorine are noisy due to a high background signal. Therefore it is difficult now to allocate the intensities directly to the polymer brush. Also the role of the catalyst species prevents definite conclusions. At about 1/3th from the right we observe an area with high intensities for chlorine which is caused by contaminations located at the surface. More contaminations are visible at the bottom of the image. At the left we observe the second structure which was etched in one direction long Z on the XY plane.

Figure A.7(b) presents the structure from a high-symmetry angle viewing along the X -axis onto the YZ plane. Tending from left to right, we obtain a higher intensity for Cl for larger Z -values towards the edge of the structure where we

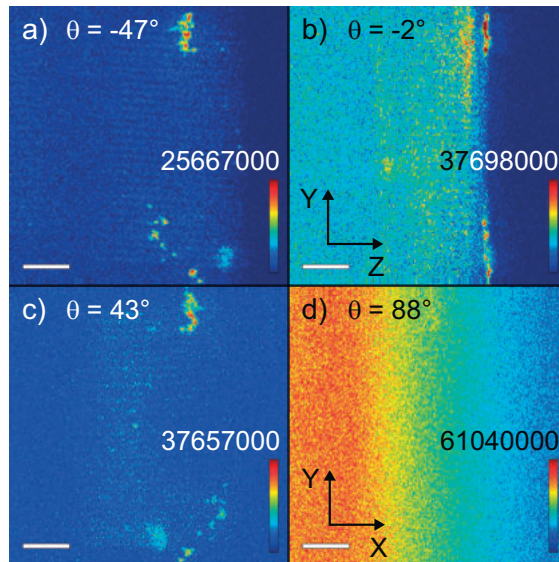


Figure A.7: Projection maps of the number of Cl atoms per pixel (area 50×50 nm) and integrated along the propagation direction of the beam, for sample orientations: a) $\theta = -47^\circ$, b) $\theta = -2^\circ$, c) $\theta = 43^\circ$, d) $\theta = 88^\circ$. Color bars with the scales are given in each panel.

expect the photonic crystal to be. Starting at about 1/3th from the right the two XY surfaces from the two structures overlap with each other resulting in high intensities for the area where the two marker and the edges of the structures overlap, we observe a high intensity.

Figure A.7(c) shows the pores along the X-axis on the left and the pores for the Z-axis on the right. The projection confirms that the chlorine signal follows the periodicity of the crystal. At about 1/3th from the right we observe an area with high intensities for chlorine which is caused by contaminations on the surface. More contaminations are visible at the bottom of the image. The marker is slightly visible on the top right.

Figure A.7(d) shows the projection onto XY plane. On the left side the edge and the YZ surface is visible. The orange area represents the pixel area for air respectively vacuum.

We conclude that the spatial resolution does not allow us to distinguish the two sources for chlorine. One important observation is that the CuCl catalyst is still present after subsequent rinsing. Furthermore it is not conclusive at this point if the brush formation was a success. We first need to have a look at the other elements to be able to further interpret the data.

By studying at the lead signal we see if the quantum dots were infiltrated into the pores. Figure A.8 shows projection maps of the number of lead atoms per pixel integrated along the sample depth at four different orientations θ . Figure A.8(a) shows the projection at $\theta = -47^\circ$. On the right we observe the 3D

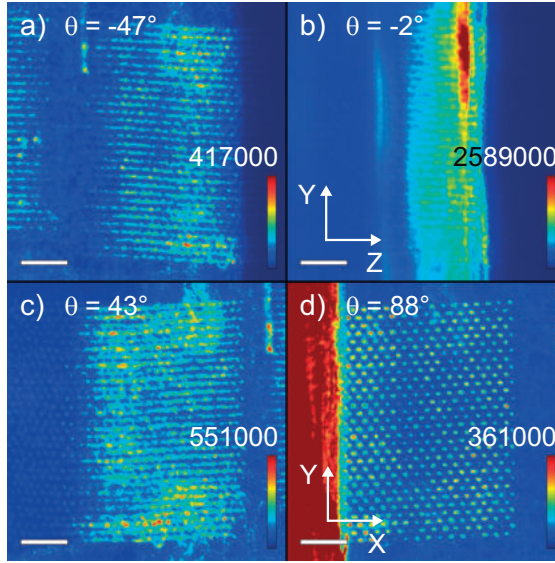


Figure A.8: Projection maps of the number of Pb atoms per pixel (area 50×50 nm) and integrated along the propagation direction of the beam, for sample orientations: a) $\theta = -47^\circ$, b) $\theta = -2^\circ$, c) $\theta = 43^\circ$, d) $\theta = 88^\circ$. Color bars with the scales are given in each panel. A high offset as been used to set the intensity bar for Figure A.8(d).

structure by viewing through the YZ plane. The periodicity of the pores is visible which means that the *quantum dots* are located inside the pores of the *photonic crystal*. This was the main moment during the synchrotron experiment that we were jumping up and down in the relief that an experiment had succeeded. Since the intensities for the Pb signal vary the deposition of the quantum dots is inhomogeneous. The marker is slightly visible at the top left. To the left we observe the second 2D structure which was etched in one direction along Z on the XY plane.

Figure A.8(b) presents the structure from a high-symmetry angle viewing along the X -axis onto the YZ plane. Tending from left to right, we see an increasing intensity with increasing Z towards the edge of the structure. Starting at about 1/3th from the right the two XY surfaces from the 3D and 2D structures almost overlap resulting in intensities on the XY surface.

Figure A.8(c) shows the pores along the X -axis on the left and the pores for the Z -axis on the right. The projection confirms that the quantum dots are inhomogeneously located along the pore length. The marker is slightly visible on the top right.

In Figure A.8(d) shows the projection onto XY plane which shows the periodicity of the pores. On the left side the edge and the YZ surface is visible. The red area represents the area for air respectively vacuum. The high intensities in this area caused a saturation of the detector that affected every element.

Figure A.9(a) shows the projection at $\theta = -47^\circ$. On the right we observe

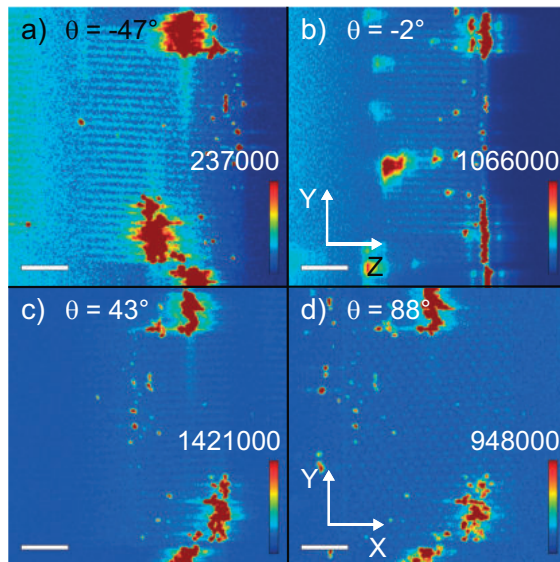


Figure A.9: Projection maps of the number of Cu atoms per pixel (50×50 nm) and integrated along the propagation direction of the beam, for sample orientations: a) $\theta = -47^\circ$, b) $\theta = -2^\circ$, c) $\theta = 43^\circ$, d) $\theta = 88^\circ$. Color bars with the scales are given in each panel.

the 3D structure by viewing through the YZ plane. Based on Figure 6.4(a) the XY plane is behind it which is not visible in this image. The periodicity of the pores is visible. Copper is present throughout the pores of the photonic crystal. The intensities for Cu varies for the area where we expect the photonic structure to be. The intensities for copper seem to be more homogeneous than lead besides the contaminations on top of the silicon bar. At about 1/3th from the right we observe an area with high intensities for copper which is caused by contaminations located at the surface. More contaminations are visible at the bottom and one the right of the image. To the left we observe the second 2D structure.

Figure A.9(b) shows the structure along the X -axis. Starting at about 1/3th from the right the two XY surfaces from the two structures almost overlap with each other. The high intensity represents the Cu atoms on the XY surface.

Figure A.9(c) shows the pores along the X -axis on the left and the pores for the Z -axis on the right. The projection confirms that copper is more homogeneously distributed than lead and we observe the periodicity of the structure. At about 1/3th from the right we observe an area with high intensities for copper which is caused by contaminations on the surface, typical of unrinsed catalyst. More contaminations are visible at the bottom of the image. Many more smaller contaminations are visible.

In Figure A.9(d) shows the projection onto the XY plane which faintly shows the periodicity of the pores etched along the Z -direction. On the left side the edge

and the YZ surface is visible. At the top of the image a spot of unrinsed catalyst on the XY surface is visible, and at the bottom a few more. The periodicity of the pores etched along Z are visible. The contrast to the area for bare silicon is low.

The signal for copper gives insight if the polymerization solution infiltrated the pores and if the chlorine surface contaminations which we observed in Figure A.7 originate from the catalyst. The presence of copper is mostly correlated to the catalyst species CuCl , whereas the correlation to Br can be neglected¹. Since we observe copper inside the pores we conclude that the polymerization solution went into the pores and got it contact with the ATRP initiator. Therefore we conclude that a polymer brush layer was grafted from the silicon-to-air interface inside the pores.

A.6 Position-resolved atomic densities

At this point we have drawn as many conclusions as possible from the projection maps of the elements. To discuss 3D position-resolved element densities, volume reconstructions are necessary. Therefore we now discuss the atomic volume densities of the elements of interest. These densities were determined from volume reconstructions for each atomic species, see Figure A.1 in the appendix. From the fitted dataset $I(E, \theta)$ (Fig. 6.4b)) we obtain the areal mass density $\rho_{a,l}$ (in units ng/mm^2) which we convert into position-resolved atomic densities $N_{v,l}$ (in units atoms/voxel volume) for each species l with

$$N_{v,l}(x, y, z) = \frac{(\rho_{a,l})MS^3N_A}{u_l}, \quad (= \text{atoms}/\text{voxel}) \quad (\text{A.4})$$

where M is the conversion from ng to g , S the spatial resolution per pixel ($S = 50 \text{ nm}$), u_l the atomic mass, and N_A the Avogadro constant.

3D nanostructure

The main text already discussed the most important results of this study including the positions of the quantum dots inside the 3D silicon photonic crystal. Here we discuss elements that provide other useful insights about the 3D nanostructure itself.

Figure A.10 shows XY cross sections of the 3D density map $N_{v,Ga}(x, y, z)$ of gallium, expressed as number of atoms per voxel where a voxel has a volume of $50 \times 50 \times 50 \text{ nm}^3$. The gallium density is first considered as it serves as a marker for the surfaces of the photonic crystal structure, therefore helping to clarify more complicated 3D density maps later on. Gallium is present at the positions where the mask of the photonic crystal was written into the chromium hard mask by focused ion beam. Figure A.10(d) shows the XY surface that

¹Since the signal for bromine originates from the monolayer which was introduced homogeneously inside the crystal structure *via* the vapor phase, we can neglect that bromine was infiltrated *via* the catalyst species. Additionally the amount of the activating catalyst species CuCl was much higher than of the CuBr_2 species.

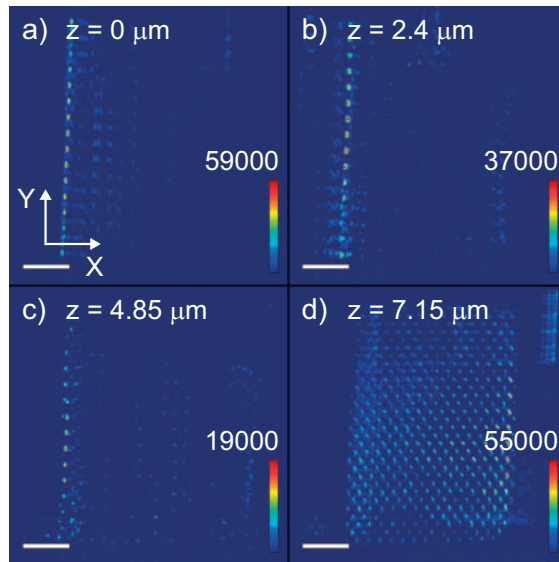


Figure A.10: XY cross sections of the reconstructed sample volume for the Ga atoms at four different depths: a) $z = 0 \mu\text{m}$, b) $z = 2.4 \mu\text{m}$, c) $z = 4.85 \mu\text{m}$, d) $z = 7.15 \mu\text{m}$.

reveals the periodic pore entrances. The marker outside the crystal is seen at the right top. We note that the cross sections deeper inside the crystal in Figure A.10(a,b,c) show hardly any spurious Ga density, thus indicating a high quality reconstruction. These cross sections show the pore entrances in the YZ surface at the left. Gallium is therefore the ideal element as a marker of the surface of the silicon photonic crystal.

Figure A.11 shows XZ cross sections of the 3D density map $N_{v,Cr}(x, y, z)$ of chromium. In Figure A.11(a) the edge of the crystal is visible at the left top based on the chromium signal. Figures A.11(b)-(d) display that on the YZ -surface for small z -values the amount of chromium present on the surface is much higher compared to the rest of the sample. The length in Z -direction for these regions is about $3.1 \mu\text{m}$. Fluorescent light signal for chromium present outside of the structure originates from artifacts of the volume reconstruction. In conclusion chromium can be used as a second marker for the silicon photonic crystal since it is only present on the surface since it was used as the hard mask for focused ion beam.

3D chemical functionalization

Figure A.12 shows XZ cross sections of the 3D bromine density map $N_{v,Br}(x, y, z)$ since bromine is expected in the ATRP monolayer as illustrated in Figure 6.1(d). In Figures A.12(a-d) we present cross sectional planes at $y = -0.05$, $y = 3.35$, $y = 6.75$ and $y = 9.85$ of the structure that will also be shown for other elements below for comparison. We observe in Figures A.12(a-d) bromine den-

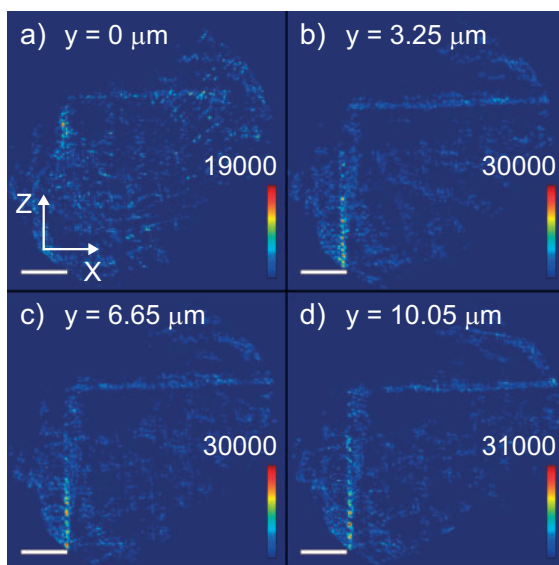


Figure A.11: XZ cross sections of the reconstructed sample volume for the Cr atoms at four different locations: a) $y = 0 \mu\text{m}$, b) $y = 3.25 \mu\text{m}$, c) $y = 6.65 \mu\text{m}$, d) $y = 10.05 \mu\text{m}$.

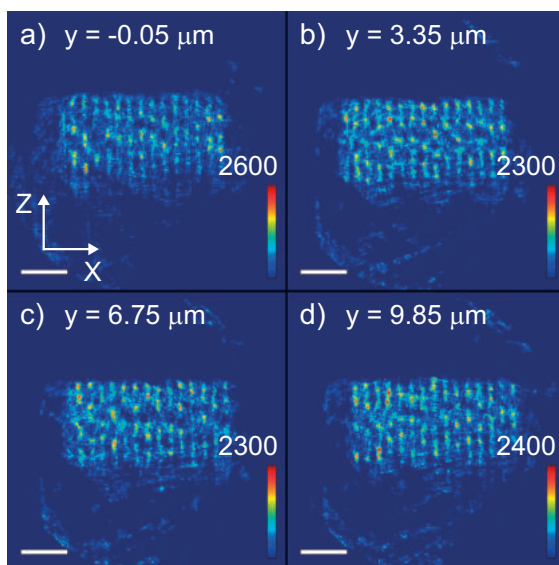


Figure A.12: XZ cross sections of the reconstructed sample volume for the Br atom density in the Z-pores at four different locations: a) $y = -0.05 \mu\text{m}$, b) $y = 3.35 \mu\text{m}$, c) $y = 6.75 \mu\text{m}$, d) $y = 9.85 \mu\text{m}$.

sity in the pores (in the Z -direction) down to a depth of $\Delta z = 3.5 \mu\text{m}$. Bromine density in the pores is visible for all pores over a width of $\Delta x = 7.2 \mu\text{m}$. For all four panels the bromine density (x, z) is very similar. We conclude that bromine is present everywhere in the pores of the 3D silicon photonic crystal. Our conclusion matches our expectations because the ATRP-initiator was introduced *via* the vapor phase.

Let us now discuss the bromine surface density inside the pores. From the fabrication point of view we assume that a typical pore of 3DPC1 has a diameter of 320 nm. This means that a pore spreads over 6 to 7 voxels in a typical cross section through a pore as seen in A.12(a-d). From the four XZ cross sections we calculate the average bromine density to be 2400 bromine atoms per voxel. This results in a total bromine density in a 50 nm high cross section of a pore of $6.5 \times 2400 = 15600$ atoms. Assuming the bromine is present on the surface of this cross section of the pores, the surface area is $2 \times 2500 \text{ nm}^2 = 5000 \text{ nm}^2$ where the area of a pixel is $50 \text{ nm} \times 50 \text{ nm} = 2500 \text{ nm}^2$. Thus we estimate the surface density to be $\frac{15600}{5000} = 3.1$ bromine atoms per nm^2 . The maximum ATRP initiator coverage that is possible for a planar surface is about 4 initiator molecules (with one bromine atom each) per nm^2 by assuming a initiator molecule width of about 0.5 nm (estimated by the bond lengths) and that the initiator molecules are standing upwards on the surface. In literature it is known from theory and experiments that the maximum initiator density for silanes on silicon is about 4 initiator molecules per nm^2 [325, 326]. Since after ATRP of the monomer that was used in excess, we expect most of the initiator molecules to transition into short polymer chains whereby the bromine is removed, the density of 3.1 bromine atoms per nm^2 seems a bit high but realistic. Based on this observation, we conclude that the ATRP-initiator formed a monolayer on the silicon-air interface. There are three more reasons to support this conclusion. Firstly, let us discuss the two possible origins how bromine can be present in the structure. Bromine can be either introduced *via* either the vapor phase deposition or *via* CuBr_2 from the catalyst species. The bromine contribution for the CuBr_2 catalyst species will later on be shown to be negligible. Secondly, the ATRP initiator does not form clusters when it is introduced *via* the vapor phase. Thirdly, the pores of the crystal were rinsed with toluene to remove excess initiator molecules from the pore surface to ensure a clean monolayer. We know from previous experiments by Leistikow and Yeganegi [289, 327] that toluene infiltrates into the pores of 3D silicon photonic crystals thus the rinsing was highly successful.

We observe in Figures A.12(a-d) variations in the bromine density along the length of the pores. Since the ATRP silane monolayer sits on the pore surface of the crystal, the bromine fluorescence signal effectively outlines the pore structure in the silicon.

Figure A.13(a-b) shows XZ cross sections of the 3D density map $N_{v,Br}(x, y, z)$ for slightly different Y -positions to visualize the pores in X -direction. We observe bromine density in the pores to a depth of $\Delta x = 2.3 \mu\text{m}$ and over a range $\Delta z = 3.9 \mu\text{m}$. The shorter pores in the X -direction are also seen in tomography data for the electron density of 3DPC1. Both Figures A.13 show a similar bromine density (x, z). We conclude that bromine density is everywhere

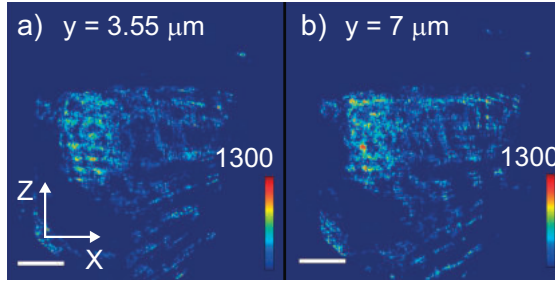


Figure A.13: XZ cross sections of the reconstructed sample volume for the Br atom density in the X -pores at two different locations: a) $y = 3.55 \mu\text{m}$, b) $y = 7 \mu\text{m}$.

throughout the pores in X -direction in agreement with the results on the deeper pores in the Z -direction in Figure A.12.

We now investigate the bromine density along the pores. Therefore, we analyze the part of the sample that is only composed of a 2D array of nanopores that run in the Z -direction, in order to avoid geometric complications due to the Br-density in the perpendicular pores. Figure A.14(a) shows the projection along Z (XY cross section) of 3DPC1 for the entire crystal volume. The right side of Figure A.14(a) shows the 2D part of the sample, where we view the pores head-on. We select all $N = 255$ Z -pores in the 2D part, and then translate the density $\rho_{Br,i}$ in each pore i to one fictitious central pore, thereby obtaining an average bromine density ρ_{Br}^{avg} within an average pore as

$$\rho_{Br}^{avg} = \sum_{i=1 \dots N} \rho_{Br,i}. \quad (\text{A.5})$$

The resulting average bromine density is shown in Figure A.14(b). The bromine density has a maximum of $5.1 \times 10^{-3} \text{ atoms/nm}^3$ at the center of the pore and decays in both the X and Y -directions, with a full width at half maximum of 300 nm in the X -direction and 180 nm in the Y -direction. From the maximum bromine density of $5.1 \times 10^{-3} \text{ atoms/nm}^3$ we estimate the bromine density per pore area once more *via* estimating the half height multiplied by the width in Δx , Δy and Δz . The number of bromine atoms is therefore $\frac{5.1 \times 10^{-3}}{\text{nm}^3} \times 300 \text{ nm} \times 180 \text{ nm} \times 50 \text{ nm} = 13770$ bromine atoms. The pore area is $50 \text{ nm} \times 2\pi \times 160 \text{ nm} = 50265 \text{ nm}^2$. We calculate the areal bromine density to be $\frac{13770}{50265} = 0.27$ bromine atoms per nm^2 . This estimate is a factor 10 below the one made above, which shows that there is a considerable error margin on the absolute density determination. Nevertheless, we will later see that our ultimate hypothesis is robust to this margin.

The peaked density distribution in Figure A.14(b) is strikingly different from our expectation, since we had expected the bromine atoms to be predominantly located as ATRP initiator near the ring-like Si-air interface, as depicted in Figure 6.1(c). Let us discuss 5 possible hypotheses for the difference.

Firstly, let us suppose that the averaged Br density in Figure A.14 suffers from a reconstruction artifact. We observe that the projected density map in

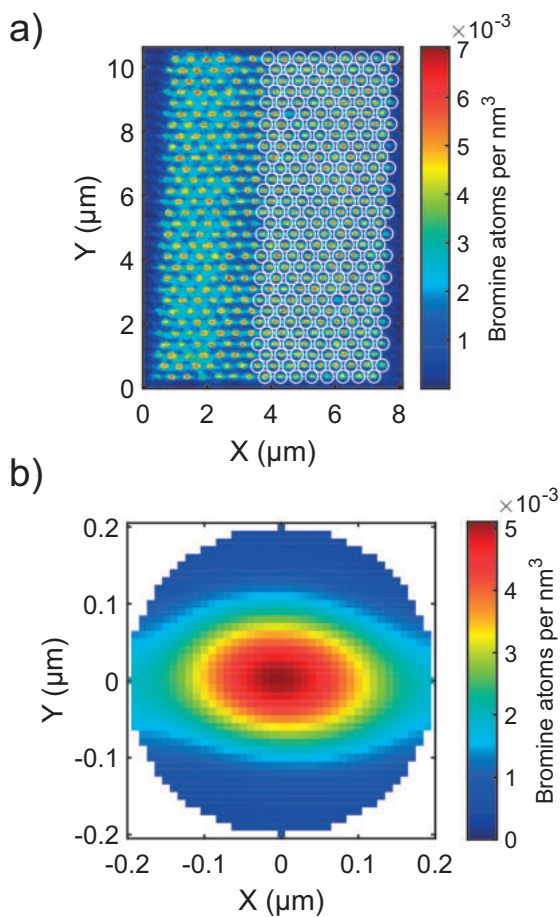


Figure A.14: Analysis of the position of the bromine atoms in the pores of the photonic crystal. a) Br density projected along the Z -direction for the entire crystal volume. The pores in the 2D crystal part are indicated by white circles. b) Br density averaged over all pores in the 2D crystal and shown in one idealized pore of average diameter 400 nm.

Figure A.14(a) is fully consistent with the measured projection map at $\theta = 88^\circ$ in Figure 6.5(d)), which is a map in a high symmetry direction similar to the projected density map in Figure A.14(a)). Therefore, we reject the hypothesis that reconstruction artifacts are relevant for the Br density.

Secondly, let us suppose that the image resolution is much worse than 50 nm due to missing angles in the image reconstruction. To verify this hypothesis, we have simulated the density that results from the expected ring-like Br-density that is convoluted with a Gaussian resolution function. We find that the resulting distribution shows ring-like behavior without central maximum even for Gaussian resolutions as coarse as 250 nm, which is highly unlikely, hence we reject this hypothesis.

Thirdly, let us suppose that the detected Br-signal does not originate from the ATRP initiator but from CuBr_2 catalyst residues that could sit on the polymer brushes. Therefore, we must also assume that the catalyst density greatly exceeds the ATRP initiator density. If there would be little initiator, there is little reason for the brush to grow from the Si-air interface in the pores. This would mean there is then little or no more reason for the PbS quantum dots to reside deep inside the pores. We reject this hypothesis firstly because the projection maps show that the ATRP monolayer is homogeneously distributed in the pores, and secondly there is evidence for polymer brushes with a chlorine density above the background outside the crystal.

Fourthly, let us suppose that CuBr_2 does not completely dissolve in the polymerization solution to form clusters, and that these large clusters sit in the pores of the crystal and could not be washed out of the structure. Since these particles must be relatively small compared to the pore diameter to easily diffuse into the pores, the statistical probability to find particles inside the pores due to gravitational settling is very low. We therefore reject this hypothesis.

Fifthly, let us suppose that the Br signal originates from washing steps with toluene to remove excess of ATRP initiator molecules from the surface. By dissolving the excess of ATRP molecules in toluene, the solution could have remained in the bottom part of the pores and the toluene could have evaporated to leave larger amounts of ATRP initiator molecules behind. At the bottom the tapering of the pores would lead to a larger projected Br density at the center of a pore. If we compare the total intensity for the bottom part of the pore with the total intensity along a pore wall (Z -pore depth about $3.5\text{ }\mu\text{m}$), we would expect a greater influence from the ATRP monolayer along the pore wall than from the bottom part of the pore. Since this does not match the observations, we reject this hypothesis.

Therefore, we conclude that at this time we have no suitable hypothesis to explain why the bromine density peaks at the center of the pores, as opposed to an expected bromine density on the pore walls. Perhaps misalignments in the projections merit future attention.

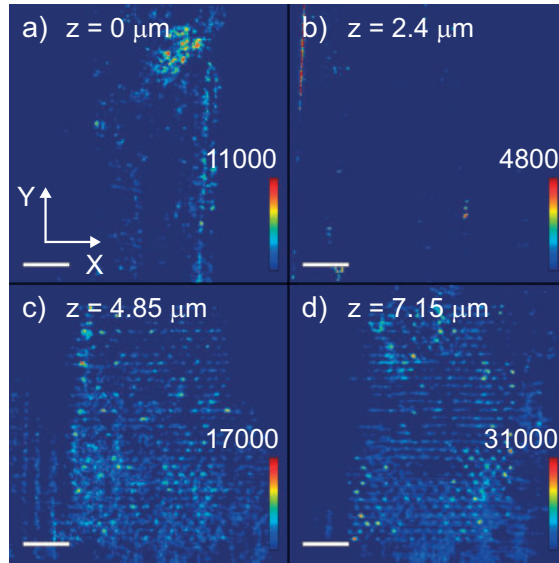


Figure A.15: XY cross sections of the reconstructed sample volume for the Pb atoms at four different depths: a) $z = 0 \mu\text{m}$, b) $z = 2.4 \mu\text{m}$, c) $z = 4.85 \mu\text{m}$, d) $z = 7.15 \mu\text{m}$.

We calculated the density of quantum dots per voxel to be between 103 (Fig. 6.7(b)) and 239 (Fig. 6.7(d))². From the number of quantum dots per voxel we derive the average distance of the quantum dots to be between 8 and 11 nm within this volume. The quantum dot density is dense and approaching the range where Förster Resonant Energy Transfer (FRET) might become apparent [328]. We assume that the PEGylated quantum dots are located at larger distances apart from each other than the threshold of FRET due to the thick polymer coating on the inorganic lead sulfide core. It is also apparent from Figures 6.7(a)-(e) that the density is inhomogeneous along the length of the pores. In panels (c), (d) there is a horizontal stripe of high density about $\Delta z = 1 \mu\text{m}$ below the YZ -surface. We observe artifacts that are attributed to the presence of the other 2D structure that was etched next to 3DPC1.

Figure A.15 shows XY cross sections of the 3D density map $N_{v,Pb}(x, y, z)$. In Figure A.15(a) the slice for the XY plane at beginning of the photonic crystal is shown for $z = 0 \mu\text{m}$. The density is low for this slice. At the top of the image a few locations are visible with a intensity up to 11000 lead atoms per voxel which corresponds to 24 quantum dots. For the depth position at $z = 2.4 \mu\text{m}$ almost no lead is visible in the pores because the cross section is below the depth of the pores which are etched along the Z -direction. Figure A.15(c) and (d) show the lead atoms in the pores of the photonic crystal and the periodic pattern. The pores are filled with PbS quantum dots for z -range which is smaller than size

²The amount of quantum dots per voxel was estimated starting with the atomic number of lead inside a voxel followed by the estimation of the number of lead atoms per quantum dot. For an average quantum dot size of 3.46 nm we estimated 465 lead atoms per quantum dot.

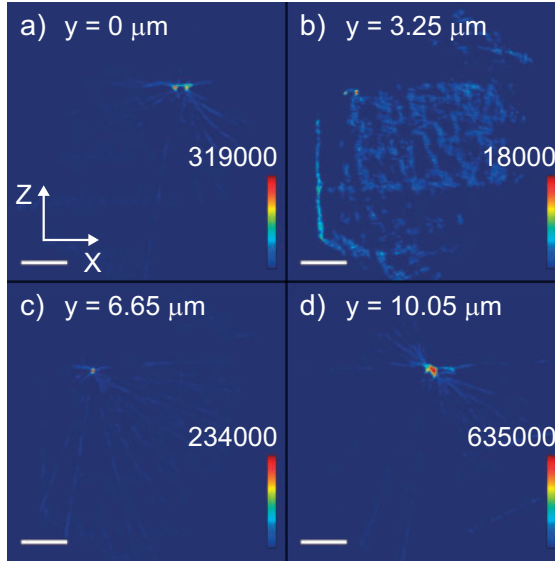


Figure A.16: XZ cross sections of the reconstructed sample volume for the Cu atoms at four different depths: a) $y = 0 \mu\text{m}$, b) $y = 3.25 \mu\text{m}$, c) $y = 6.65 \mu\text{m}$, d) $y = 10.05 \mu\text{m}$.

which was expected for the photonic crystal from the fabrication design. Close to the surface of the XY plane we observe a maximum lead intensity of 31000 lead atoms per voxel which corresponds to 67 QDs per voxel volume. We observe a higher density on the surface compared to the maximum inside the pores which means that the quantum dots are located on average at smaller distances from each other due to surface agglomeration.

Figure A.16 shows XZ cross sections of the 3D density map $N_{v,Cu}(x, y, z)$. We observe in Figure A.16(a), (c) and (d) areas with high amount of copper atoms per voxel which is most likely caused by contaminations on the surface. In Figure A.16(b) a square of the photonic crystal structure is visible. On the left side a thin line is visible which is the surface of the YZ -plane. Since the periodicity is not visible by looking at the reconstruction data, the amount of atoms for copper is summed for each slice to make the periodicity visible (see Fig. A.17).

Figure A.17 shows the number of copper atoms summed for each slice plotted against the Y -position. Between $3.5 \mu\text{m}$ and $9 \mu\text{m}$ the periodicity ($a/2$) of the photonic crystal is visible. For the other locations the contaminations are dominant which leads to a large signal such that the periodicity is not visible anymore. That is why an intensity range between 0 and 2.5×10^7 is chosen to display the copper inside the pores of the crystal. We calculate the copper density to be $\frac{3 \times 10^6}{7.2 \times 10^9} \frac{\text{atoms}}{\text{slice}} \times 50 \text{ nm}^3 \times 6.5 = 341$ copper atoms per slice. Therefore the areal density is $\frac{341 \text{ atoms}}{5000 \text{ nm}^2} = 0.068 \frac{\text{atoms}}{\text{nm}^2}$. If we now take the density ratio between bromine ($3.1 \text{ atoms per nm}^2$) and copper ($0.068 \text{ atoms per nm}^2$) we observe that the copper density is around 46 times too low for the bromine signal to

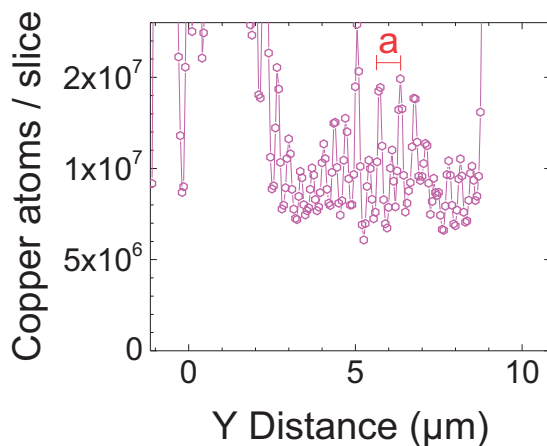


Figure A.17: Number of copper atoms per slice present in 3DPC1 (magenta hexagons) plotted against the Y distance. The a parameter of the photonic crystal is presented in red.

be determined by the catalyst species. It is chemically possible that during the polymerization and the subsequent rinsing, the copper and bromine have split such that the anion could have remained in the polymer brush while the copper was rinsed away. We cannot further judge at this point how much that would influence the data. Therefore we conclude that the bromine signal stems from the ATRP initiator. We confirm herewith our assumption that the copper was infiltrated into the pores by the polymerization solution. As mentioned above, this observation confirms the successful ATRP of poly(glycidyl methacrylate) inside the pores of 3DPC1.

We summarize the element densities observed in 3DPC1 in the following table A.3.

Table A.3: Element densities for every species found in the structure. For each element an averaged density was calculated from the four projection maps that were shown earlier.

element	atoms per slice
Bromine	1.0×10^5
Chlorine	4.1×10^7
Chromium	1.2×10^6
Copper	9.2×10^5
Gallium	7.1×10^5
Lead	9.8×10^5

B Detailed sample properties

In Table A.4 we present the properties of the silicon photonic crystals that we etched into the individual silicon beams.

Table A.4: Properties of the photonic crystals that were etched into the individual silicon beams. The column "Sample name in the text" gives the sample name that was used in the text, column "Sample name in the lab" the sample name that is used in our group and column "Remarks" further details on the fabrication and the properties of each photonic crystal.

Sample name in the text	Sample name in the lab	Remarks
3DPC1	PG-EBAR-30032017-CH4B	Silicon bar with 14 photonic crystals fabricated with the single-step etch mask process described in Ref. [206, 207]. The silicon bar is coated with a thin polymer brush layer of poly(glycidyl methacrylate) to which PbS-PEG-NH₂ quantum dots are attached. Crystals: S1: 2D, $d = 260$ nm, no cavity (nc); S2: 2D, $d = 230$ nm, nc; S3: 2D, $d = 230$ nm, nc; S4: 3D, $d = 320$ nm, with cavities; S5: 3D, $d = 320$ nm, nc; S6: reference structure; S7: 2D, $d = 260$ nm, nc; S8: 3D, $d = 260$ nm, nc; S9: 3D, $d = 260$ nm, nc; S11: 3D, $d = 320$ nm, nc; S12: 3D, $d = 320$ nm, nc; S13: 2D, $d = 320$ nm, nc; S14: 2D, $d = 320$ nm, nc; S15: $3 \times 2D$, $d = 260$ nm, nc.
3DPC2	PG-EBAR-30032017-CH3B	Silicon bar with 5 photonic crystals fabricated with the single-step etch mask process described in Ref. [206, 207]. The silicon bar is coated with a thin polymer brush layer of poly(glycidyl methacrylate). PbS-OA quantum dots are dip-coated onto the sample. Crystals: S1: 3D, $d = 320$ nm, nc; S2: 3D, $d = 260$ nm, nc; S3: 3D, $d = 260$ nm, nc; S4: 2D, $d = 260$ nm, nc; S5: $3 \times 2D$, $d = 320$ nm, nc.

C Normalization factors

In Table A.5 we present the normalization factors to scale each measured relative intensity spectra such that the peak at 10800 cm^{-1} matches the calculated one in the corresponding DOS spectrum (see Figure 7.2 in Chapter 7.)

Table A.5: Scale factors of the measured relative intensity spectra compared to the calculated DOS spectra, taken at the peak at 10800 cm^{-1} .

Structure name	Normalization factor
C8	2.1
C9	2.3
C12	5.0
C4	16.7
C5	27.9

A limitation to our calibration procedure is, of course, that the theoretical results pertain to an infinite crystal, hence the inhibition is perfectly 0 and the gap has sharp bounds, whereas the observed inhibition is rounded and finite. Based on the variations in the spectra, we estimate the error margins of the scale factors above, and the concomitant relative intensities, to be about 10% relative error.

D Excited-state lifetime measurements

In Table A.6 we present all the excited-state lifetime measurements that were performed on our samples.

Table A.6: Results of the excited-state lifetime measurements on sample 3DPC1, 3DPC2 and a dip-coated silicon bar. The column "Measurement position" gives the details about the location of the measurement, column " Γ_{mf} in μs^{-1} " the decay rate Γ_{mf} , column " $\Delta\Gamma$ " the distribution width and column " χ^2_{red} " the goodness-of-fit.

Measurement position	Γ_{mf} in μs^{-1}	$\Delta\Gamma$	χ^2_{red}
3DPC1			
QD suspension	0.223 ± 0.004	1.09(3)	1.083
flat: 50 μm above S12	190.3 ± 0.6	290 ± 4	1.087
flat: 75 μm above S12	267.0 ± 0.6	348 ± 4	1.171
flat: 100 μm above S12	258.4 ± 0.6	336 ± 4	1.136
S3 (2D)	257.4 ± 1.6	527 ± 11	1.024
S4 (3D)	173.0 ± 2.8	1200 ± 300	1.047
S5 (3D)	177.0 ± 2.1	1080 ± 230	1.108
S12 (3D)	153.0 ± 1.3	780 ± 130	1.070
S4 (3D), exception	10.6 ± 0.2	67 ± 22	1.057
3DPC2			
QD suspension	1.0175 ± 0.0004	0.0(7)	1.019
QD-cluster	1.34 ± 0.13	13.6 ± 2.1	1.155
flat: 30 μm above S1	8.18 ± 0.05	117.3 ± 2.4	1.233
flat: 50 μm below S4	11.929 ± 0.017	96.1 ± 0.5	1.706
flat: 70 μm below S4	11.771 ± 0.019	109.0 ± 0.7	1.821
S1 (3D)	70 ± 40	700 ± 700	0.987
MK-Nano PbS			
QD suspension	1.1280 ± 0.0008	0.314 ± 0.015	1.003
MK-Nano dip-coated	11.67 ± 0.05	16.17 ± 0.14	1.015

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Nederlandse samenvatting

Het is uit de kwantummechanische theorie bekend dat de invloed van fotonische bandkloofkristallen op de spontane emissie van ingebouwde kwantumemitters - zoals halfgeleider-kwantumdeeltjes - gevoelig afhangt van de locatie waarin de emitters zich bevinden. Het is daarom een grote uitdaging om methoden te ontwikkelen die precieze plaatsing van emitters in fotonische kristal-nanostructuren mogelijk maken. Dit proefschrift gaat deze uitdaging aan door middel van moderne chemische methodologieën: wij bestuderen hoe kwantumdeeltjes met polymeerborstels kunnen worden gepositioneerd in een fotonisch kristal. Daarom hebben we een geschikte oppervlaktechemie *via* silaan-monolaagvorming, polymeerborstels en de covalente hechting van loodsulfide-kwantumdeeltjes met een geschikt organisch ligand onderzocht. De kennis die we aanvankelijk verkregen uit vlakke siliciumsubstraten werd gebruikt als input om geavanceerde methoden voor de fabricage van complexe 2D en 3D fotonische kristal-nanostructuren van silicium te ontwikkelen.

We hebben aangetoond dat het polymeer met zorg moet worden gekozen om de laagdikte van de op silicium gehechte polymeerborstels te kunnen sturen. Door te kiezen voor poly(*N*-isopropylacrylamide)-lagen werd een precieze controle over de laagdikte bereikt, met name door het variëren van de activerende en deactiverende katalysatordeeltjes. In het geval van poly(glycidyl-methacrylaat) waren we in staat om de laagdikte van het polymeer te controleren door middel van de polymerisatietijd. Aangezien het groeien van poly(glycidyl-methacrylaat)-borstels betrouwbaarder bleek te zijn, besloten we om met dit epoxide-bevattende polymeer verder te gaan.

Voor het precies positioneren van kwantumpunten in de poriën van 3D fotonische kristallen van silicium was het nodig om een uitgebreide strategie voor de oppervlaktechemie te ontwikkelen. Aangezien we gekozen hadden voor PGMA-lagen was een geschikt organisch ligand op de loodsulfide-kwantumdeeltjes belangrijk. We lieten daartoe de epoxide-zijgroepen van PGMA reageren met amino-PEG-gefunctionaliseerde loodsulfide-kwantumdeeltjes. Door de koppelingsomstandigheden te variëren verkregen we dichtgepakte kwantumdeeltjes gehecht aan PGMA-borstels.

Nabij-infrarood emitterende kwantumdeeltjes werden in dit proefschrift bestudeerd omdat hun geëmitteerde fotonen niet worden geabsorbeerd door het hoofbestanddeel (silicium) van onze 3D fotonische bandkloofkristallen. We kozen loodsulfide-kwantumdeeltjes voor onze experimenten omdat deze commercieel verkrijgbaar waren met verschillende organische liganden.

Suspensies van kwantumdeeltjes werden bestudeerd om spectra en tijdopgeloste emissiesnelheden van de nanokristallen te meten. Wij vergeleken de vervalsnelheden van de loodsulfide- kwantumdeeltjes in suspensie met een model voor een ideaal exciton op twee niveaus.

Om de ontwikkelde oppervlaktechemie toe te passen, moesten we ervoor zorgen dat we een schoon siliciumoppervlak verkregen na de fabricage van de fotonische siliciumkristallen. Wij werden geconfronteerd met het probleem dat er na de fabricage van onze fotonische siliciumkristallen fluorkoolstofresten aanwezig waren op de poriewanden van de kristallen. Deze versturende verontreinigingen moesten worden verwijderd door middel van intensieve reinigingsstappen. Onze reinigingsprocedure, bestaande uit RCA-2-reiniging en een oxidatiestap bij 800 °C in een oven, leidde tot ultraschone fotonische siliciumkristalmonsters die konden worden gebruikt voor het functionaliseren met kwantumdeeltjes door middel van geavanceerde oppervlaktechemie.

Een hoogtepunt van dit proefschrift zijn de experimentele studies verkregen uit synchrotronexperimenten verricht bij de European Synchrotron Radiation Facility (ESRF) in Grenoble. De fotonische kristallen van silicium werden geanalyseerd met röntgentomografie om de elektronendichtheid te bepalen, zoals beschreven in het proefschrift van Grishina [206]. Met behulp van röntgenfluorescentietomografie zijn wij erin geslaagd om de chemische samenstelling van onze kristallen te analyseren. Voor zover wij weten zijn wij de allereersten die experimentele gegevens hebben verkregen van siliciumnanostructuren die zijn gedoteerd met kwantumdeeltjes waarvan de posities werden gecontroleerd door polymeerborstels. We hebben de sterke punten en voordelen van röntgenfluorescentietomografie in vergelijking met andere technieken gepresenteerd. Na gedetailleerde analyse van de verkregen gegevens is inzicht verkregen in de kwantumdeeltjesbedekking in de poriën van de fotonische kristallen. Bovendien konden we de onderscheidende broomatomen van de ATRP-initiatormoleculen en de chlooratomen van de polymeerborstels karakteriseren.

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Andreas
2025 - Enschede

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